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1 Geology of the Don Manuel igneous complex, central Chile:  
2 implications for igneous processes in porphyry copper systems

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10  
11 **ABSTRACT**

12 The Don Manuel igneous complex (DMIC) and associated porphyry copper mineralization in the  
13 Andean Cordillera of central Chile demonstrates similarities between intrusive complexes  
14 associated with porphyry copper deposits (PCDs) and arc volcanoes that generate porphyritic  
15 volcanics. The DMIC intrusions progressed from quartz monzonite through rhyolite and biotite  
16 tonalite, to intermediate porphyritic and basaltic andesite dikes which intrude the older units.  
17 Mineralization is associated with the biotite tonalite and intermediate porphyries, which also  
18 contain the greatest abundance of mafic enclaves. Zoning patterns within plagioclase phenocrysts  
19 suggest that the later intermediate porphyries comprise a hybridized suite formed by magma  
20 mixing. New zircon U-Pb ages and whole rock Ar-Ar ages indicate that the DMIC was emplaced  
21 between ca. 4 and 3.6 Ma. The timescale for the episodic intrusion of the DMIC units is similar to  
22 observed episodicity of eruption and degassing events in active arc volcanoes. Observations from



the DMIC are consistent with the close spatial and temporal association of mineralization with both episodic intrusion and interaction between silicic and mafic magmas during emplacement. The observations are also consistent with the hypothesis that mafic magma provides a source of sulfur for porphyry copper deposit formation.

## **INTRODUCTION**

Porphyry copper deposits (PCDs) form in association with high-level hypabyssal dikes or stocks, which are commonly referred to as “sub-volcanic” (Gustafson and Hunt, 1975; Hedenquist and Lowenstern, 1994; Redmond et al., 2004; Sillitoe, 1973, 2010). These mineralized intrusions are thought to be connected to larger pluton-scale magma reservoirs at depth and many have suggested a genetic or physical connection with volcanoes (Sillitoe, 1973, 2010; Sinclair, 2007). Volcanoes in convergent plate margin settings and PCD-related intrusions are typically characterized by calc-alkaline, water-rich and oxidized magmas (Kelley and Cottrell, 2009; Richards, 2011) that form rocks with porphyritic textures (Cline and Bodnar, 1991; Sillitoe, 2010) and often exhibit evidence of magma mixing (Halter et al., 2005; Lickfold et al., 2007; Murphy et al., 1998). The petrological similarity of many arc volcanic rocks and hypabyssal porphyry intrusions is well established (Dilles, 1987; Halter et al., 2004; Longo et al., 2010; Maydagán et al., 2011; Sillitoe, 1973; Waite et al., 1997). The igneous connection is particularly well demonstrated in the Yerington district, Nevada, where mineralized dike swarms are rooted in a granite pluton and exposures extend into the overlying contemporaneous volcanics (Dilles, 1987).

Direct temporal and spatial volcanic-PCD connections are difficult to establish due to the spatial distance between the volcanic edifice on the surface and the formation of porphyry copper deposits typically at depths of 1 to 6 km (Seedorff et al., 2005). Volcanic edifices are not preserved where

erosion rates are high and associated rocks have been hydrothermally altered. Where evidence for direct connections is lacking, other criteria must be used to compare the evolution of the igneous systems associated with arc volcanoes and those associated with PCD formation.

Recent advances in understanding intermediate to silicic volcanic and plutonic systems show periods of eruption and intense degassing occur on timescales of years to centuries, and are interspersed with dormant periods lasting thousands to tens of thousands of years (Christopher et al., 2015; Harford et al., 2002; Hildreth et al., 2003; Le Friant et al., 2008). Relevant to the interpretation of intrusions associated with porphyry copper deposits, is the emerging evidence from geochronology and thermal and diffusion modelling for the highly episodic assembly of shallow crustal calc-alkaline plutons (Annen et al., 2015; Mercer et al., 2015; Tapster et al., 2016) on timescales similar to those of eruptive and degassing periods observed at active volcanoes. Important questions are: (1) whether PCD-related hypabyssal intrusive complexes are formed by processes similar to the processes that form sub-volcanic conduit systems that supply arc volcanoes; and (2) how do these processes relate to mineralization?

This paper is the first description of the geology, geochronology, and geochemistry of the Don Manuel igneous complex (DMIC), associated with one of the youngest known porphyry copper systems in the Andes. The complex is situated in the Miocene-Pliocene porphyry copper belt of central Chile, between the giant El Teniente porphyry copper-molybdenum deposit and the active Maipo volcano (Fig. 1). Although destructive hydrothermal alteration occurs locally in the DMIC, there are many areas with weak to no alteration, enabling primary magmatic features associated with a porphyry copper system to be investigated. We describe the units of the DMIC, including their geological relationships, geochemical compositions, ages, and evidence for magma mixing and mingling. We consider the similarities between the DMIC and arc magmas, in particular the

episodic character of arc volcanism and hypabyssal igneous complexes to highlight the potential role of mafic magma in PCD genesis and discuss the links between magmatic degassing, hypabyssal intrusion and mineralization.

## **GEOLOGIC SETTING**

### **Regional Geology**

The Don Manuel igneous complex is located in the Andean Cordillera of the O'Higgins Region of Chile, approximately 100 kilometers southeast of Santiago and 30 km southeast of the giant El Teniente porphyry copper-molybdenum deposit (Fig. 1). Tectonically, the DMIC sits within the South American plate in the Principal Cordillera. This area is part of the northern segment of the Southern Volcanic Zone (NSVZ). The NSVZ has been studied extensively to understand the dynamics of subduction-related magmatism (Dungan et al., 2001; Hildreth and Moor bath, 1988; Kay et al., 2005; Kay et al., 1991; Stern and Skewes, 1995). Moreover, the region has been the focus of intense research on porphyry copper deposits, as it is part of the central Chile Miocene-Pliocene metallogenic belt (Atkinson Jr et al., 1996; Cannell et al., 2005; Deckart et al., 2005; Hollings et al., 2005; Kay and Kurtz, 1995; Kurtz et al., 1997; Maksae v et al., 2004; Muñoz et al., 2012; Piquer et al., 2015; Reich et al., 2003; Serrano et al., 1996; Skewes and Stern, 1995; Stern et al., 2007; Stern and Skewes, 1995; Stern et al., 2011; Vry et al., 2010; Warnaa rs et al., 1985).

Just north of the DMIC and the NSVZ is the Chilean flat-slab segment (29°S-33°S) (Kay et al., 2005; Marot et al., 2014; Stern and Skewes, 1995) where the Nazca plate is subducting below the South American plate at an angle of ~10° (Farías et al., 2010; Yáñez et al., 2002). The marked change in subduction style compared with areas to the north and south has been attributed to subduction of the Juan Fernandez Ridge (JFR), which began at around 25 Ma and has progressively

91 moved southward (Yáñez et al., 2002; Yáñez et al., 2001). The flat slab region between 28° and  
92 33°S lacks active arc volcanoes, whereas south of latitude 33°S, the slab subducts at ~30° (Fig.1)  
93 (Marot et al., 2014; Pardo et al., 2002; Yáñez et al., 2002), and active arc volcanism is represented  
94 by several Late Pliocene to Holocene volcanic centers. Near the 33°S change in slab dip, the flat  
95 slab may increase crustal compression and reduce asthenospheric mantle wedge temperatures in  
96 the NSVZ, resulting in lower magma production rates and longer ascent and residence times than  
97 areas of the SVZ further to the south underpinned by steeper subduction angles (Marot et al., 2014).

98 Magmatic activity in central Chile began in the Jurassic and was relatively stable until the Pliocene,  
99 at which point the arc progressively moved eastward to its current position (Camus, 2003; Kay et  
100 al., 2005; Stern, 2004; Stern and Skewes, 1995). Between the late Eocene and the late Oligocene,  
101 an extensional basin opened and was filled with lavas, volcanoclastic and lacustrine sediments of  
102 the Abanico Formation, equivalent to the Coya Machalí Formation further to the south (Charrier  
103 et al., 2002; Charrier et al., 1996; Godoy et al., 1999; Kay et al., 2005) and later by volcanic units  
104 of the Miocene Farellones Formation (Charrier et al., 2002; Kay et al., 2005; Vergara et al., 1988).

105 In most areas of central Chile, the Farellones Formation unconformably overlies the Coya Machalí  
106 Formation. It ranges in age from 25 to 7.4 Ma (Vergara et al., 1988) and consists of up to 2,400 m  
107 of gently folded andesitic to rhyolitic lavas and volcanoclastic sequences (Charrier et al., 2002;  
108 Nyström et al., 2003). In the area of the DMIC (~34°20'S) it can be difficult to distinguish between  
109 the Farellones and Coya Machalí formations, as the volcanic sequences are very similar in  
110 composition and the contact between the two is transitional (Charrier et al., 2002). Both the Coya  
111 Machalí Formation and the lower member of the Farellones Formation have bimodal compositions  
112 and were emplaced during periods of extension, whereas the upper Farellones Formation formed  
113 during passive to mild contraction (Nyström et al., 2003). The Young Plutonic Complex, which

includes predominantly granodiorite intrusions, ranging in age from 6.6 to 5.5 Ma (Kay et al., 2005; Kurtz et al., 1997), marks the eastward frontal migration of the arc.

The DMIC and associated porphyry copper prospect occur in country rock consisting of mostly basaltic andesite lavas and volcanoclastic deposits interbedded with fluvial and lacustrine sedimentary units of the Coya Machalí Formation (Fig. 2). The formation is up to 2,500 m thick and late Eocene to early Miocene in age (Kay and Kurtz, 1995). Locally the sequence is strongly folded and locally metamorphosed to lower greenschist facies (Godoy et al., 1999).

Structurally, the DMIC sits on the eastern edge of the late Eocene to late Oligocene Coya Machalí extensional basin (also known as the Abanico basin) (Farías et al., 2010). Godoy et al. (1999) suggested that the Coya Machalí basin was inverted in the late Oligocene to early Pliocene, resulting in folds and out-of-sequence thrust faults and uplift. Basin inversion appears to have been syn-depositional with both the Coya Machalí and Farellones formations, and shortening was accommodated primarily by reactivation of the original extensional basin-bounding faults (Godoy et al., 1999; Charrier et al., 2002; 2007). The DMIC lies just west of the El Fierro fault system, one of the major reactivated basin-bounding faults (Candia et al., 2009; Godoy et al., 1999).

Regional deformation has been characterized by over 63 km of shortening in three main events (Farías et al., 2008; Farías et al., 2010; Giambiagi and Ramos, 2002). Inversion of the Abanico basin around 22 to 15 Ma was followed by development of a thin-skinned fold-and-thrust belt in the eastern Principal Cordillera between 16 and 8.5 Ma and then by uplift of the Frontal Cordillera and thrust faulting in the eastern Principal Cordillera between 8.5 and 4 Ma. Late Miocene thrust faulting was contemporaneous with migration of magmatic activity to the west (Farías et al. 2010).

The closest active Holocene volcanic center to the DMIC is the stratovolcano Maipo, ~25 km to the northeast (Fig. 1). Maipo volcano sits within the much larger Diamante Caldera formed by eruption of rhyolitic ignimbrites ~450,000 years ago (Hynek et al., 2010). In the Cerro de la Laguna area just east of the Diamante Caldera, lavas, ignimbrites and lahar deposits record pre-caldera, volcanic activity dating to the Late Miocene (Sruoga et al., 2012; Sruoga et al., 2005).

#### **Central Chile Miocene-Pliocene porphyry copper-molybdenum belt**

The central Chile Miocene-Pliocene porphyry copper-molybdenum belt extends from approximately 32°S to 34°S along the western flank of the Principal Cordillera and consists of N-S (orogeny-parallel) aligned deposits of Miocene to Pliocene age; this belt hosts three of the world's largest porphyry copper deposits: El Teniente, Río Blanco-Los Bronces, and Los Pelambres-El Pachón (Fig. 1). The PCDs in this belt are hosted in multiple porphyritic intrusions and late magmatic-hydrothermal breccias (Atkinson Jr et al., 1996; Cannell et al., 2005; Deckart et al., 2005; Makshev et al., 2007; Serrano et al., 1996; Warnars et al., 1985). These porphyritic intrusions formed toward the end of a tectonic-magmatic cycle that began around 19 Ma and are considered to be the last gasp of magmatism prior to the eastward shift of the volcanic front to the present-day location (Kay et al., 2005; Skewes and Stern, 1995; Stern, 2004; Stern et al., 2007).

The association of this belt of world-class PCDs and associated intrusions that have adakite-like geochemical characteristics (Defant and Drummond, 1990; Kay, 1978; Loucks, 2014; Richards and Kerrich, 2007) has been explained by several different models. By definition, adakites have high Sr/Y and La/Yb in intermediate calc-alkaline igneous rocks (Defant and Drummond, 1990; Kay, 1978; Richards and Kerrich, 2007). They have been attributed to either partial melting of the down-going oceanic slab (Defant and Drummond, 1990, 1993; Kay, 1978; Oyarzun et al., 2001) or mid- to deep-crustal fractionation of amphibole and/or garnet, involving wet (>4% H<sub>2</sub>O),

oxidized basalts/andesites (Castillo, 2012; Chiaradia, 2015; Richards, 2011; Richards and Kerrich, 2007; Zellmer et al., 2012). Changes in the residual mineralogy from plagioclase to amphibole  $\pm$  garnet to produce the adakite-like signature may be the consequence of increased crustal thickness and resulting changes in the magma source region and may have supplied additional water for PCD formation (Kay and Mpodozis, (2001).

## **ANALYTICAL TECHNIQUES AND SAMPLING METHODS**

The study area is divided into two parts, the northern Paredones area and the southern Don Manuel Principal area where 8 holes were drilled to explore for porphyry copper deposits (Fig. 3). Dikes and small stock-like intrusions dominate outcrops in the Paredones area, but moraines, alluvium, and glaciers cover much of the complex in the Don Manuel Principal area. This study is therefore based on fieldwork in the Paredones area and logging of drill cores from the Don Manuel Principal area.

Over 350 representative samples of the various intrusive and country rocks were collected from the surface exposures in the Paredones area and the eight drill cores. Samples collected were variably altered and were selected to characterize the original igneous textures and mineralogy as well as the products of alteration associated with sulfide mineralization. A fresh to minimally altered sub-set of these samples was selected for focused characterization of the primary mineral assemblage, compositions, and sample textures. Samples were examined petrographically using both transmitted and reflected light, as well as by scanning electron microscopy (SEM) at the University of Bristol.

Whole rock major and trace elements were analyzed for 78 samples by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry

(ICP-MS) at the Element Analysis Facility at Cardiff University (Table 1 and Supplementary material DR1 and Table DR1) following the procedures documented in McDonald and Viljoen (2006). For the purpose of identifying the primary igneous characteristics of the DMIC, only the least altered samples were used and visible veins were removed prior to analysis (see Table DR1 for alteration intensity). Total sulfur analyses of all 78 samples and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  by iron titration analysis for a selected sub-set of 12 samples was performed at Acme Analytical Laboratories Ltd., Canada.

Quantitative plagioclase analyses were carried out using a Cameca SX100 electron microprobe at the University of Bristol. Analyses were performed using a 20 kV, 10 nA beam for major elements and a 100 nA beam for minor and trace elements (Table 2 and Table DR2). Counting times for most elements were 30s on peak and 15s on the background. Sodium mobility was not observed when Na was measured first. Minor and trace elements in plagioclase were analyzed using counting times of 40-120 s on peak for Sr, 40-200s for Ba, 90-150s for Fe, and 50-300s for Mg. A labradorite standard was run as an unknown at the beginning of each session. The results for these standards and all analyses are presented in Table DR2.

Zircon fractions from nine DMIC samples were analyzed at the NERC Isotope Geosciences Laboratory at the British Geological Survey by CA-ID-TIMS methods to determine  $^{238}\text{U}$ - $^{206}\text{Pb}$  dates (Table 3 and DR3). Zircons were separated from bulk rock samples using standard separation techniques. Grains chosen for CA-ID-TIMS were imaged under transmitted light and fractions with the fewest inclusions were selected. Additional zircons were mounted in epoxy, polished and imaged by cathodoluminescence (CL) techniques to assess the complexity of the zircon growth histories. As many of the DMIC zircons are small (~50-300  $\mu\text{m}$ ) and have low concentrations of radiogenic Pb, we favored dating whole zircons or fragments rather than those where volume had



been reduced by polishing for CL imaging. Zircons selected for analysis by CA-ID-TIMS were thermally annealed and chemically abraded following the methods of Mattison (2005). Analysis of DMIC samples is technically challenging, requiring a robust uncertainty model for the common Pb isotopic composition and extremely low common Pb laboratory blanks (average 0.6 pg) and due to the small sizes of zircons (<150  $\mu\text{m}$ ), their low U concentrations (typically <200 ppm for the intermediate porphyry dike zircons) and the young age of the DMIC. All dates are reported in millions of years (Ma);  $2\sigma$  uncertainties are noted in the form of  $\pm x/y/z$ , where x is the analytical uncertainty suitable only for inter-comparison of U-Pb within this study and other EARTHTIME tracer ID-TIMS dates, y is the uncertainty inclusive of tracer calibration, and z is the total uncertainty, including  $^{238}\text{U}$ - $^{206}\text{Pb}$  decay constant (Jaffey et al., 1971), required for comparison with dates yielded by additional isotopic systems, e.g.,  $^{40}\text{Ar}/^{39}\text{Ar}$ . Full analytical methods, procedures and data handling are described in detail in supplementary material DR3.

Don Manuel Principal basaltic andesite groundmass separates were analyzed using  $^{40}\text{Ar}/^{39}\text{Ar}$  method at the NERC Ar Isotope Facility (Table 4). Samples were crushed, sieved, and purified using a combination of magnetic separation and mild leaching in dilute  $\text{HNO}_3$ . Altered grains and/or phenocrysts were removed by hand picking under a binocular microscope. Additional analytical methods and procedures are described in detail in supplementary material DR4 and complete raw data reported according to Renne et al. (2009) are given in Table DR4.

## **DON MANUEL IGNEOUS COMPLEX**

Don Manuel has been a prospect of recent interest for exploration as a consequence of its proximity to other major ore deposits such as El Teniente and the occurrence of similar indicators of hypogene PCD mineralization. We have focussed our study on this complex because locally there

is excellent preservation of primary igneous textures. Thus DMIC provides a remarkable opportunity to study the higher temperature igneous processes associated with mineralization that are commonly masked by the effects of strong alteration in many PCDs.

Six main intrusive/hypabyssal units have been recognized in the DMIC. Four of these units occur in the Don Manuel Principal area (Fig. 2 and Fig. 3) in the southern part of the study area. These include: quartz monzonite; biotite tonalite, a stock-like body which is volumetrically the most significant rock type; a suite of intermediate porphyry dikes; and basaltic andesite dikes which cross cut the other units. In all eight drill cores, these igneous units are hosted by the Coya Machalí Formation, which consists of volcanic and volcanoclastic deposits interbedded with fluvial and lacustrine sedimentary units. The biotite tonalite, intermediate porphyry dikes and Coya Machalí Formation crop out at the surface (Candia et al., 2009). In the Paredones area (Fig. 3), two additional igneous units were recognized: a rhyolite stock and basaltic andesite dikes. These units are also hosted by the Coya Machalí Formation (Fig. 3).

The DMIC in both the Don Manuel Principal and Paredones areas is locally extensively altered. Within the drill cores, the alteration intensity varies and is locally discontinuous. Calc-silicate intervals in the Coya Machalí Formation have largely been altered to garnet-clinopyroxene-epidote skarn and a clinopyroxene-magnetite-actinolite-epidote skarn; other siliciclastic sedimentary facies, volcanoclastic facies, and volcanic hornfels exhibit secondary biotite adjacent to the biotite tonalite and intermediate porphyry dikes and more distally contain chlorite and epidote (Fig. 4A). Along the northwestern contact of the rhyolite in the Paredones area, the host rocks have been intensely hornfelsed and locally the rhyolite stock has been silicified.

Observed copper sulfides in the core from the Don Manuel Principal area are primarily hosted in the biotite tonalite, intermediate porphyry dikes, and sedimentary and volcanoclastic hornfels and skarn lithologies of the Coya Machalí Formation. The copper grades of the DMIC rocks are commercially confidential, but confirm the strong association of mineralization with the biotite tonalite and IPDs (Candia et al., 2009). Within the igneous units, copper sulfides occur in porphyry-style veins (Fig. 4B) and disseminated in the host rock. In the skarns, copper sulfides are massive, whereas they are disseminated and vein-hosted in the surrounding sedimentary and volcanoclastic hornfels. No copper sulfides were observed in the Paredones area.

Three main stages of mineralization and alteration can be recognized: an early stage characterized by silicification and pervasive magnetite and secondary biotite associated with K-silicate alteration; a primary mineralization stage, characterized by vein-hosted chalcopyrite associated with K-silicate alteration and distal propylitic alteration including abundant chlorite and actinolite; and a late mineralization stage of lower temperature produced localized chlorite-sericite and sericite and argillic alteration assemblages. The close temporal association of the peak mineralization with the major intrusions documented below has been confirmed by Re-Os dating of molybdenite in mineralized veins (Gilmer, 2016). A detailed account of the mineralization will be presented elsewhere.

## **Don Manuel Principal units**

### ***Quartz monzonite***

The quartz monzonite (67-74 wt. % SiO<sub>2</sub>) is fine- to medium-grained and locally porphyritic, and composed of plagioclase, microcline, quartz, and biotite (Fig. 4C). Accessory minerals include apatite, magnetite, and rutile. Where porphyritic, plagioclase phenocrysts range in size from 1 to 3.5 mm, and primary biotite phenocrysts are 0.5 to 1.3 mm (Fig. 5A and Fig. 6A). The quartz

monzonite occurs in short vertical intervals (less than 20 m) in two drill holes (DM2 and DM6) and is crosscut by intermediate porphyry and basaltic andesite porphyry dikes. Overall, this unit has a fine-grained equigranular groundmass, and locally, it is also strongly silicified and contains disseminated secondary biotite with minor secondary magnetite. In other narrow intervals, vein-related sodic-calcic alteration is characterized by growth of actinolite and magnetite and albitization mostly within vein selvages. Disseminated pyrite and pyrite veinlets are the only sulfides present in the quartz monzonite. Based on the absence of copper sulfides, and because this unit is cut by the intermediate porphyry dikes that have the most sulfide minerals and veins, it is interpreted to be pre-mineralization (Fig. 3B).

#### ***Biotite tonalite***

The biotite tonalite (64-68 wt. % SiO<sub>2</sub>) is the most common unit, observed in drill cores DM2, DM4, DM7, and DM8. Overall, this intrusion is medium- to coarse-grained, with typical plutonic texture, and has horizontal dimensions of at least 1.5 km. It constitutes over 80% of the 600 m of drill hole DM4. Drill holes DM7 and DM4 both terminate in biotite tonalite; with DM4 ending in brecciated biotite tonalite. Two textural varieties of biotite tonalite were identified in the drill core, one equigranular and one porphyritic (Fig. 4D and 4E). Drill holes DM4 and DM7 contain intervals of both varieties. Contacts between the two are rare, but where observed are sharp.

The biotite tonalite ranges from medium- to coarse-grained and is composed of subhedral to anhedral plagioclase, tabular biotite, microcline, quartz, and  $\pm$  amphibole (Fig. 5B and 5C); small (0.5-1 mm) aggregates of quartz, plagioclase, biotite, and microcline are also present (Fig. 6B). Accessory minerals include apatite, anhydrite, titanite, magnetite, ilmenite, and zircon; however, the titanite is anhedral suggesting that this phase is secondary. The porphyritic biotite tonalite (Fig. 4E) contains plagioclase (1-4 mm), biotite (1-3 mm), and amphibole (1-4 mm long) phenocrysts.

The groundmass in the porphyritic phase has an intergranular texture comprising crystals ranging from 0.2-0.3 mm. Anhydrite inclusions are present in plagioclase in both variants. Mafic enclaves are common throughout the biotite tonalite (Fig. 4D) and show chilled margins where the hotter, more mafic magma cooled against the biotite tonalite. Crosscutting relationships indicate that the biotite tonalite is older than the intermediate porphyry dikes and basaltic andesite dikes (Fig. 3B).

The biotite tonalite contains pyrite, chalcopyrite and molybdenite in quartz veinlets with sericite halos, and disseminated in the interstitial space adjacent to quartz, biotite, and anhydrite. With the exception of the rare anhydrite inclusions in plagioclase, anhydrite occurrences are likely secondary. Later veins and cavities, primarily within the porphyritic phase, contain coarse-grained anhydrite, biotite, quartz and molybdenite, but no other sulfides. In the majority of core intercepts, the biotite tonalite is mineralized.

The biotite tonalite unit shows both propylitic and K-silicate alteration. Within the propylitically-altered zones, chlorite has replaced biotite, actinolite has replaced amphibole and plagioclase has been replaced by sericite, epidote and/or calcite. K-silicate alteration is characterized by pervasive secondary biotite replacing primary biotite and amphibole, and patchy areas (10-50  $\mu\text{m}$ ) of potassium feldspar replacing plagioclase. Relict amphiboles contain abundant titanite and rutile, which may be the result of late magmatic alteration of titanomagnetite or alteration of amphibole to biotite, the remaining titanium forming titanite and rutile.

### ***Intermediate porphyry dikes***

Numerous intermediate porphyry dikes intrude the biotite tonalite and Coya Machalí Formation. This suite of dikes shows a wide range of textures and modal compositions, ranging from dacite to andesite (59-68 wt. %  $\text{SiO}_2$ ) (Fig. 4B and 4F). These porphyries vary from less than one to 60

meters in width, and occur in all drill cores (DM1-DM8). The distribution of textural types is spatially complex, and the suite displays sharp contacts as well as gradational contacts. Where the contacts are sharp, they dip steeply at  $\sim 10^\circ$  to  $25^\circ$  to the subvertical drill core orientation. These sharp contacts may separate dikes of nearly identical composition or dikes of a distinctly different texture and composition within the intermediate suite. Contact-parallel flow foliations are common adjacent to these sharp contacts. Numerous features of magma mixing are observed in these dikes, including mafic enclaves and irregular contacts (Fig. 6F and Fig. 7). In some cases, undulating contacts suggest intrusion of one dike into partially solidified magma of another dike.

The intermediate porphyry dike phenocryst contents range from 30 to 60 modal %. The main phenocrysts are euhedral plagioclase (0.3-2 mm),  $\pm$  subhedral to euhedral amphibole,  $\pm$  biotite (0.2–2 mm), and  $\pm$  quartz (0.2–1 mm) (Fig. 5C). The intermediate dikes can be divided into three types on the basis of the ferromagnesian phenocryst assemblage. Type 1 contains primary biotite phenocrysts, but no amphibole (Fig. 5D), Type 2 contains both primary biotite and amphibole phenocrysts (Fig. 5E), and Type 3 contains amphibole phenocrysts, but no biotite (Fig. 5F). Two of the Type 1 intermediate porphyry dikes also contain trace amounts of rounded and embayed quartz phenocrysts. The groundmass consists of plagioclase, amphibole,  $\pm$  biotite, and quartz. Anhydrite inclusions in plagioclase were observed in all three types of intermediate porphyry dikes, although they are rare ( $n=5$ ). Accessory minerals include apatite, titanite, magnetite, ilmenite, and zircon.

The intermediate porphyry dikes contain more copper than any other unit (based on commercially confidential assays, BHP Billiton personal communication, January 2014). Disseminated chalcopyrite, bornite, and pyrite occur within all three types of intermediate porphyry dikes; the dikes also contain veins and veinlets of quartz  $\pm$  chalcopyrite-pyrite-bornite-specularite-

337 molybdenite; quartz  $\pm$  chalcopyrite; quartz  $\pm$ pyrite; quartz-chlorite $\pm$  actinolite-pyrite; quartz-  
338 anhydrite  $\pm$  chalcopyrite-pyrite-molybdenite; and quartz-molybdenite  $\pm$  anhydrite.

339 The intermediate porphyry dikes show selective replacement of both amphibole and primary  
340 biotite by titanite, hydrothermal biotite, magnetite and sulfides. In some cases, the dikes exhibit  
341 chlorite, actinolite, and epidote replacement of biotite and amphibole, and minor sericite  
342 replacement of plagioclase phenocrysts. Overall, the alteration in the intermediate porphyry dikes  
343 has preferentially affected the groundmass and ferromagnesian phases. Many of the intermediate  
344 porphyry dikes also contain miarolitic cavities filled with quartz, apatite, anhydrite, epidote, and  
345 calcite, and some cavities also contain chalcopyrite and pyrite.

#### 346 ***Basaltic andesite dikes***

347 The Don Manuel Principal basaltic andesite dikes are the most mafic unit in the Don Manuel drill  
348 core (54-57 wt. % SiO<sub>2</sub>). These dikes occur as short vertical intervals in all of the drill cores (DM1-  
349 DM8) and are typically less than 10 meters in thickness; they have near-vertical contacts with other  
350 units (Fig. 4G). The basaltic andesite dikes crosscut the intermediate porphyries. They are  
351 aphanitic to porphyritic with up to 20% phenocrysts (Fig. 5G). Where porphyritic, the main  
352 phenocrysts are euhedral to subhedral plagioclase (0.2–1.5 mm) and euhedral to subhedral,  
353 prismatic amphibole (0.2–1.3 mm) (Fig. 6E). Phenocrysts adjacent to dike contacts show contact-  
354 parallel alignment. The groundmass contains plagioclase, amphibole and biotite, with accessory  
355 apatite, titanite, magnetite and ilmenite (Fig. 5E). As seen in the intermediate porphyry dikes,  
356 several dikes also contain circular or irregular miarolitic cavities (1-5 mm diameter) infilled with  
357 quartz, anhydrite, apatite, biotite, and pyrite.

Pyrite is the only sulfide present in the basaltic andesite dikes; it occurs as pyrite veinlets, and pyrite + quartz veinlets, and disseminated. The basaltic andesite ranges from completely unaltered to weakly altered; in the altered dikes primary amphibole has been replaced by actinolite, and chlorite. Epidote and calcite may also locally occur in these dikes. They are interpreted to be late- to post-mineralization dikes.

## **Paredones units**

### ***Rhyolite porphyry***

The rhyolite porphyry crops out in the northeastern corner of the Paredones field area, forming a ~1 km<sup>2</sup> subcircular, stock-like outcrop geometry (Fig. 3A). The rhyolite is predominately porphyritic; however, silicification has locally destroyed this texture, and is associated with abundant fractures. Prominent limonite (after pyrite) staining is observed. Where the primary texture is intact, the main phenocrysts comprise plagioclase (0.8-3.5 mm), biotite (0.3-2.5 mm), and rare quartz “eyes” (0.3-0.6 mm) (Fig. 6G and Fig. 8). Accessory minerals include apatite, titanite, and zircon. Secondary pyrite is locally disseminated. The rhyolite also contains rare mafic enclaves. Basaltic andesite porphyry dikes cut the rhyolite; the contacts are undulose and embayed (Fig. 8), typical of mafic intrusions into hot ductile silicic host rock (Blake et al., 1965). No copper minerals were observed in this unit.

### ***Basaltic andesite dikes***

Several vertical NW-SE striking dikes of basaltic andesite crop out in the Paredones area (Fig. 3). They are the most mafic unit in the study area (54-55 wt. % SiO<sub>2</sub>). The dikes have a porphyritic texture with up to 60% phenocrysts, including plagioclase (0.1-1.5 mm), clinopyroxene (0.2 to 2 mm), biotite (0.3-1 mm) and minor amphibole ( $\leq 0.5$  mm); the groundmass has the same mineralogy (Fig. 5h and 7). In places, the groundmass has a subophitic texture with plagioclase



laths enclosed by clinopyroxene. The presence of clinopyroxene phenocrysts distinguishes these basaltic andesite dikes from those encountered in the drill core. Samples collected adjacent to and cutting the rhyolite are strongly and pervasively altered; chlorite has completely replaced all ferromagnesian phases. Dikes that cut the volcanoclastic units of the Coya Machali Formation are considerably less altered. No copper minerals were observed in this unit.

## **WHOLE ROCK COMPOSITIONS**

### **Major and trace elements**

The DMIC samples contain between 53 and 74 wt. %  $\text{SiO}_2$  (Table 1; Table DR1; Fig. 9). The mafic enclaves have  $\text{SiO}_2$  contents between those of the intermediate porphyry dikes and the basaltic andesite dikes. The DMIC samples follow a typical calc-alkaline trend and are metaluminous to peraluminous (Irvine and Baragar, 1971; Shand, 1951). Some mobile elements such as K, Na, Rb, and Cs show variation that is likely to be related to alteration. Although there is scatter in the compositions of the basaltic andesite dikes, mafic enclaves, and intermediate porphyry dikes, linear compositional trends are clear for most major oxides (Fig. 10). Within the DMIC, as  $\text{SiO}_2$  increases,  $\text{TiO}_2$ ,  $\text{FeO}^*$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MgO}$ , and  $\text{CaO}$  all decrease (Fig. 10). Overall  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  increase with increasing  $\text{SiO}_2$ , although these components show more scatter, which is attributed to hydrothermal alteration. Alteration intensity for whole rock geochemical samples is noted in Table DR1 and alteration type is noted where justified.

Chondrite-normalized rare earth element (REE) patterns (Sun and McDonough, 1989) are similar across all samples and show patterns typical of subduction-related magmas (Pearce and Peate, 1995; Tatsumi, 1989). All DMIC samples show enrichment of Light REE (LREE) with respect to Heavy REE (HREE) (Fig. 11) and have similar ranges in REE abundances, however the

intermediate porphyries and mafic enclaves show the most variability. DMIC REE patterns show very little fractionation between the Middle REE (MREE) and HREE. Most samples in the DMIC do not show a negative Eu anomaly. Many of the DMIC units have high Sr/Y and La/Yb, the biotite tonalite and some intermediate porphyry dike samples in particular, and plot in the “adakite” fields of Defant and Drummond (1993) and Castillo et al. (1999) (Fig. 12). The less evolved samples of the DMIC have signatures more typical of arc rocks.

## **MAGMA MINGLING AND MIXING**

### **Mafic enclaves and hybridization textures**

Field, core and geochemical observations reveal conspicuous igneous contacts, structures and textures indicative of magma mingling, mixing and hybridization associated with the DMIC. Mafic enclaves can be found within the rhyolite, equigranular biotite tonalite, and in the intermediate porphyry dikes (Fig. 4D and 5A). These enclaves range in length from <1 cm to 15 cm, although intercepts within the drill core may not capture their full dimensions. Enclave morphologies range from subspherical to elongate and may have diffuse margins. They are most abundant in the biotite tonalite and intermediate porphyry dikes. Within the biotite tonalite enclaves can occur in clusters, which may represent intersections with enclave-rich syn-plutonic intrusions that are commonly attributed to dismemberment of a mafic dike intruded into a hot ductile pluton (Furman and Spera, 1985; Hallot et al., 1996) (Fig. 4D). Enclaves vary from aphanitic to porphyritic; phenocrysts consist of plagioclase, hornblende (often altered to secondary biotite), and biotite. The groundmass of the enclaves consists mainly of plagioclase and biotite with minor quartz.

Many of the enclaves display diktytaxitic textures, and some contain miarolitic cavities (Fig. 6D). Diktytaxitic textures likely result from exsolution of volatiles and consequent undercooling leading

to rapid crystallization (Bacon, 1986; Blake and Fink, 2000; Sparks and Marshall, 1986). Contacts between the enclaves and host can be crenulated and undulating or may show a more abrupt fine-grained chilled margin. In several instances, a phenocryst (plagioclase or hornblende) straddles the contact between the enclave and the host or appears to have become almost completely entrained by the enclave (Supplementary material Figure DR5.1). These are all classic features of mafic inclusions generated by mingling of mafic and more silicic magma (Bacon, 1986; Sparks and Marshall, 1986; Tepley et al., 2000; Vernon, 1984).

Within some intermediate porphyry dikes, there is evidence that interaction between the two magmas was more extensive, resulting in a more thoroughly mixed, hybridized texture (Fig. 7B). Amphibole crystals occur as glomerocrysts within the enclaves and as microenclaves within the adjacent host. These mafic clots (1 to 3 mm) may also include primary plagioclase, biotite, titanite, and magnetite. Amphibole crystals are euhedral to subhedral and range in size from 1 to 3 mm. These clots likely originated from disintegration of larger mafic enclaves (Humphreys et al., 2009). The enclaves are commonly more altered (in the form of secondary biotite, epidote and chlorite) than their hosts because they contain additional ferromagnesian phases (Supplementary material Figure DR5.1). The mineralogical changes are consistent with the observed depletion in CaO and MgO and elevated K<sub>2</sub>O and Na<sub>2</sub>O values in some of the mafic enclaves (Fig. 10).

#### **Plagioclase zoning and phenocryst assemblages**

Plagioclase is the most common mineral in all of the DMIC units. Importantly, plagioclase zones preserve the original magmatic compositions and crystallization conditions because of sluggish, coupled substitution of the Si and Al pair (Grove et al., 1984). This attribute can be used to infer mixing between the magmas of different units and to determine whether this mixing involved a

mafic magma and/or was caused by convective self-mixing from hotter recharge magma of the same composition (Couch et al., 2001; Humphreys et al., 2009; Streck, 2008).

Plagioclase phenocrysts from the Paredones rhyolite show the simplest zoning patterns, with minor variations and little or no resorption (Fig. 13). All plagioclase phenocrysts in this unit show normal zoning and have cores of An<sub>28-45</sub> and rims of An<sub>6-28</sub>. Plagioclase phenocrysts from the basaltic andesite dikes show minor normal zoning and little or no resorption, and have cores of An<sub>75-85</sub> and rims of An<sub>50-70</sub> (Fig. 13). In both of these units, the rim compositions are the same as the surrounding groundmass plagioclase.

In contrast, plagioclase phenocrysts from the intermediate porphyry dikes show complex zoning and resorption surfaces as well as diverse assemblages within a single dike. Five distinct types of plagioclase phenocrysts were identified in the intermediate porphyry on the basis of optical and SEM characteristics and electron microprobe analyses. Plagioclase phenocrysts selected for study are unaltered (no albitization) and all zones are interpreted to be magmatic. These include: (1) reversely zoned plagioclase phenocrysts that have broad cores of An<sub>23-38</sub> and sieve-textured rims with sharp transitions to An<sub>51-56</sub> (Fig. 14); (2) oscillatory zoned phenocrysts that have high amplitude, high frequency variations in An content, cores of An<sub>21-44</sub> and rims that are normally zoned, An<sub>51-32</sub>; (3) patchy zoned phenocrysts containing An<sub>48-58</sub> cores showing significant resorption and rims that are An<sub>49-32</sub> (Fig. 14); (4) largely unzoned, euhedral grains that have cores of An<sub>51-58</sub> and rims of An<sub>50-37</sub>; and (5) patchy zoned phenocrysts commonly in glomerocrysts, having cores of An<sub>87-66</sub> and rims of An<sub>50-28</sub> (Fig. 14). All five types of plagioclase phenocrysts can be found within single thin sections of the intermediate porphyry dikes.

## **GEOCHRONOLOGY**

A well-constrained chronology is a prerequisite for interpreting the durations of igneous processes and emplacement frequencies associated with the formation of PCDs, as well as for placing a deposit in the context of regional tectonics. We have employed both high-precision CA-ID-TIMS U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronological methods to provide time constraints for the DMIC.

### **U-Pb geochronology**

Samples from the quartz monzonite (n=2), rhyolite (n=1), equigranular biotite tonalite (n=1), porphyritic biotite tonalite (n=1) and the intermediate porphyry dikes (n=4) were chosen for CA-ID-TIMS U-Pb dating. Dates and isotopic compositions of single zircon fractions are listed in Table 3 and weighted mean dates are presented in Figure 15 for grains of euhedral and elongate shapes, which showed no resorbed cores in CL images. Multifaceted grains were avoided where possible as these were shown to contain resorbed zones comparable to those discussed in Tapster et al. (2016), and therefore do not represent zircon growth upon emplacement. Both weighted mean dates and the youngest single fraction dates show a clear temporal progression that agrees with observed crosscutting relationships where observed. Best estimates for emplacement ages are interpreted from the weighted mean dates of the youngest clusters of zircon  $^{238}\text{U}/^{206}\text{Pb}$  dates that form statistically acceptable mean squared weighted deviations (MSWDs) at the 95% confidence interval.

From the quartz monzonite, five zircons from DM6AG05 yielded a weighted mean date of  $4.040 \pm 0.015/0.016/0.016$  Ma with an MSWD of 2.26 and six zircons from DM2AG33 yielded a weighted mean date of  $3.975 \pm 0.057/0.058/0.058$  Ma with an MSWD of 1.2. Type 3 intermediate porphyry dike DM6AG21 yielded two clusters of dates, with a weighted mean of  $4.058 \pm 0.036/0.060/0.060$  Ma (n=6; MSWD of 1.48) for the older cluster, and a weighted mean date (n=2) of  $3.912 \pm 0.057/0.066/0.066$  Ma for the younger cluster that we take as our preferred emplacement

age. Rhyolite (DMN30) yielded a weighted mean date of  $3.879 \pm 0.017/0.018/0.018$  Ma (MSWD=0.5, n=6). The equigranular biotite tonalite (DM2AG01) yielded a weighted mean date of  $3.829 \pm 0.009/0.010/0.011$  Ma (MSWD=0.6, n=11) whereas the porphyritic biotite tonalite (DM4AG14) yielded a weighted mean date of  $3.733 \pm 0.012/0.012/0.013$  Ma (MSWD=0.9, n=7). Six zircons from a Type 1 intermediate porphyry dike, sample DM8AG44, yielded a weighted mean date of  $3.733 \pm 0.048/0.050/0.050$  Ma (MSWD of 1.5) which is closely comparable to that of DM4AG16. Six zircons from DM5AG32, a Type 2 intermediate porphyry dike, yielded a weighted mean date of  $3.656 \pm 0.028/0.029/0.029$  Ma with an MSWD of 1.0 and DM3AG15, another Type 2 intermediate porphyry dike, yielded a near identical weighted mean date of  $3.657 \pm 0.031/0.032/0.032$  Ma with an MSWD of 1. Zircon xenocrysts, with dates of ca. 8 Ma and ca. 5 Ma were noted in samples, DM2AG33, DMN30, DM8AG44 and DM3AG15 (Table 3).

#### **$^{40}\text{Ar}/^{39}\text{Ar}$ geochronology**

Two groundmass separates from the Don Manuel Principal basaltic andesite dikes were step heated using the  $^{40}\text{Ar}/^{39}\text{Ar}$  method (see supplementary material DR4 for method details). The Paredones basaltic andesite dikes have not been dated. Samples analyzed are interpreted to be dikes that cross-cut either older volcanoclastic units or the equigranular biotite tonalite. Table 4 summarizes the geochronologic data and gives results for total fusion ages and inverse isochron ages in Ma. Plateau acceptance criteria are at least four consecutive age steps that are indistinguishable at the  $2\sigma$  level and represent 50% or more of the total  $^{39}\text{Ar}$  released during the experiment. The scatter between these steps should be low (MSWD approaching 1); for plateaus with excess scatter (MSWD>1), the uncertainty on the plateau age is multiplied by the square root of MSWD. Values for MSWD were below the cut-off criteria outlined in Wendt and Carl (1991) and no error expansion was applied. Furthermore, the trapped component derived from an inverse isochron analysis should be

indistinguishable from atmospheric composition. Samples DM4AG28 and DM7AG26 satisfied these criteria.

Sample DM7AG26 has a plateau age of  $3.60 \pm 0.06$  Ma (Fig. 16A). This basaltic andesite dike cross cuts sedimentary hornfels. Sample DM4AG28, which was emplaced in the biotite tonalite, has a plateau age of  $3.85 \pm 0.19$  Ma (Fig. 16B). This result is within uncertainty of the zircon U-Pb age for the equigranular biotite tonalite, and although it was interpreted as a small contemporaneous dike, it could also be a larger (relative to the drill core) mafic enclave.

## **DISCUSSION**

### **Evolution of the Don Manuel Igneous complex**

The DMIC represents a suite of hypabyssal and upper parts of plutonic intrusions, which like other porphyry copper-related intrusions, was emplaced within the upper crust (Cooke et al., 2014; Seedorff et al., 2008; Seedorff et al., 2005). Overall, the DMIC shows a temporal progression from dominantly silicic magmas with very minor mafic components (enclaves and intermediate dikes) to more mafic magmas represented by porphyritic intermediate and basaltic andesite dikes (Fig. 17). We attribute this trend to the tapping of progressively deeper parts of the transcrustal magmatic system (Cashman et al., 2017) together with mafic replenishment. Based on the new U-Pb dates, the silicic magmas in this system lasted for  $\sim 400$  kyr (Fig. 17) beginning at ca. 4 Ma. The  $3.85 \pm 0.19$  Ma and  $3.60 \pm 0.06$  Ma Don Manuel Principal basaltic andesite dikes and the presence of mafic enclaves within the rhyolite, biotite tonalite, as well as evidence for magma mixing in the intermediate porphyry dikes, document the periodic emplacement of mafic magma into the upper crust throughout the lifetime of this magma system (Fig. 4 and Fig. 7).

Fractionation of the DMIC magmas occurred deeper than the level of final intrusion, under varying physical conditions. LREE enrichment, HREE depletion, a dip of MREE relative to HREE (Fig. 12) can be explained by fractionation of amphibole (Davidson et al., 2007). The high Sr/Y ratio and negligible Eu anomaly in the biotite tonalite and intermediate porphyry dikes ( $\text{Eu}/\text{Eu}^* = 0.7\text{--}1.2$ ), and the small Eu anomaly in the rhyolite ( $\text{Eu}/\text{Eu}^* = 0.68\text{--}0.84$ ), is attributed to suppression of plagioclase crystallization during magma evolution under high  $p\text{H}_2\text{O}$  and presumably deeper conditions (Moore and Carmichael, 1998; Müntener et al., 2001). Both the biotite tonalite and many of the intermediate porphyry dikes contain amphibole phenocrysts, which suggests relatively high water content ( $\geq 4$  wt. %  $\text{H}_2\text{O}$ ; (Naney, 1983; Richards, 2011; Richards et al., 2012). Within the intermediate porphyry dike suite, variations in Sr/Y and La/Yb suggest different amounts of amphibole fractionation prior to onset of plagioclase crystallization (Castillo, 2012; Castillo et al., 1999). A negligible Eu anomaly could also result from high oxidation conditions (e.g. Dilles et al., 2015). Primary anhydrite inclusions in plagioclase in the biotite tonalite and intermediate porphyry dikes are consistent with relatively oxidized magmas (NNO +1 to NNO +3) (Carroll and Rutherford, 1987; Luhr, 1990; Matjuschkin et al., 2016; Scaillet et al., 1998). We infer that the negative Eu anomaly reflects both high  $p\text{H}_2\text{O}$  and high oxidation conditions.

## **Episodic igneous processes and mineralization**

Both PCDs and volcanoes are the top or near top expressions of upper crustal magma reservoirs (e.g. Dilles, 1987; Lipman, 2007; Scandone et al., 2007; Tapster et al., 2016). The DMIC developed over a timescale comparable to many arc volcanoes, contains a similar wide range of magma compositions, shows evidence of deeper fractionation of oxidized wet magmas, and displays features indicative of magma mixing and mingling. Although we cannot be sure that the DMIC connected directly to a volcano, it is reasonable to infer that volcanoes and porphyry-



associated hypabyssal intrusive complexes share some processes of magma ascent and degassing from deeper in the crust. The specifics of these dynamic processes, however, determine whether or not an ore deposit forms.

We first consider time scales as defined by the geochronology, geology of the intrusions, thermal constraints and observations at active arc volcanoes. High-precision geochronological studies and thermal modelling suggest that volcanic and shallow intrusive systems in arcs are highly pulsatory (Annen et al., 2015; Michel et al., 2008; Sparks and Cashman, in press). Volcanic dome complexes are, for example, characterized by short periods of extrusive activity fed by dikes separated by much longer periods of repose. Dome complexes and stratovolcanoes typically have durations of many hundreds of thousands of years (e.g. Clavero et al., 2004; Harford et al., 2002; Hoshizumi et al., 1999), comparable to the ca. 400 kyrs duration of the DMIC. Many arc volcanoes are characterized by highly episodic bursts of volcanic activity that last years to perhaps a few centuries and are separated by dormant periods lasting thousands to tens of thousands of years (e.g. Hildreth and Lanphere, 1994; Le Friant et al., 2008). In the Maipo volcanic center, ~25 km northeast of DMIC, the large-volume eruption that produced the Diamante ignimbrite was followed by a period of ca. 350 kyr. dormancy prior to post-caldera reactivation, during which eruptive episodes occurred on the order of every 30 kyrs or less (Sruoga et al., 2005; Stern et al., 1984).

Likewise, shallow intrusions in arcs involve multiple short bursts of intrusion separated by long periods of inactivity (Barboni et al., 2015; Caricchi et al., 2012; Michel et al., 2008; Miller et al., 2011). For example, emplacement of the Torres del Paine laccolith in Chile occurred in discrete, short-lived pulses over  $90 \pm 30$  kyrs, with large time gaps between pulses (Leuthold et al., 2012; Michel et al., 2008). Thermal modelling (Annen et al., 2015) indicates that single pulses at Torres

del Paine lasted only hundreds of years at most. Other examples of episodic pluton emplacement together with thermal modeling constraints are discussed in Barboni et al. (2015) and Annen et al. (2015).

Cross-cutting relationships and age data indicate that the development of the DMIC was also highly episodic. Based on our U-Pb ages and their  $2\sigma$  uncertainties (Figs. 15 and 17) the time intervals between emplacement of the major units are constrained to the order of 10's kyrs to ~100 kyrs:  $95 \pm 59$  kyrs ( $2\sigma$ ) (quartz monzonite and rhyolite),  $51 \pm 19$  kyrs ( $2\sigma$ ) (rhyolite and equigranular biotite tonalite), and  $96 \pm 15$  kyrs ( $2\sigma$ ) (biotite tonalite and porphyritic biotite tonalite).

With the exception of the biotite tonalite and the rhyolite, the numerous intrusions of DMIC are dikes that have widths of meters to tens of meters at most. Conductive cooling times would range from 1-10 years for meter scale dikes to  $10^3$  years for the 1500 m diameter rhyolite stock (Jaeger et al., 1968). Emplacement times must be even shorter. These cooling times are orders of magnitude shorter than the minimum age differences between the major intrusive units, thus indicating that each unit would have solidified before the emplacement of the next intrusive unit. The minimum time intervals between the quartz monzonite and the rhyolite stock and between the rhyolite and the equigranular biotite tonalite intrusions are both constrained to ca. 30-35 kyrs (Fig. 17) and the different textural facies of the biotite tonalite (equigranular and porphyritic) have distinctive ages, indicating a minimum time interval of ca. 80 kyrs. It is most probable, that this represents the accumulation of multiple yet discrete magmatic pulses similar to the emplacement of Torres del Paine, as cooling models would require an intrusion diameter of at least 2 km to emplace the biotite tonalite over a duration of 80 kyrs or more (Annen, 2009). The observed sharp contacts suggest, however, that two short-lived intrusive pulses of compositionally similar but

texturally contrasted magma is a more plausible explanation.

Conductive cooling times constrain the emplacement of individual hybrid porphyritic dikes of the DMIC to be very short ( $<1$  to  $10^2$  years), comparable to the typical time scales for emplacement of feeder dikes associated with porphyritic lava dome eruptions (years to decades). In addition, composite dikes observed in DMIC have undulose contacts (Supplementary material, Figure DR6), recording the pulsed behavior of magma injection that must occur at timescales more rapid than those defined by cooling (i.e. still ductile at the time of the next intrusion). The processes causing pulsatory dike emplacement in the DMIC may be similar to those that lead to repetitive cyclic lava dome extrusion over periods of weeks to years in many dike-fed lava dome eruptions (Sparks, 1997). Composite dikes were, for example, encountered during the drilling of the Mt. Unzen volcanic conduit that formed between 1991 and 1995 (Goto et al., 2008).

Pulsed porphyritic intrusions are a feature of PCDs elsewhere. The tens kyrs timescales documented for the DMIC are similar to those documented by Tapster et al. (2016) in the Koloula porphyry copper deposit in the Solomon Islands and by Buret et al. (2016) in the Bajo de la Alumbrera porphyry copper deposit in Argentina. Additionally, detailed, high-resolution U-Pb geochronology from other PCDs has shown that the entire duration of igneous activity associated with mineralization episodes can be short, lasting only a few hundred thousand years or less and that this activity is also episodic (Buret et al., 2016; Chelle-Michou et al., 2015; Tapster et al., 2016; Von Quadt et al., 2011). As more high-precision data sets emerge from other studies of geologically well-constrained PCDs such episodic igneous activity may become a well-recognized feature of porphyry copper systems.

626 The spatial distribution and timing of mineralization are closely associated with hypabyssal  
627 intrusions at DMIC, as is also the case at many other PCDs (e.g. Dilles (1987) and Spencer et al.  
628 (2015)). Intrusions can create the pathways for mineralization fluids from deeper magma systems.  
629 Observations of dike rocks and volcanic systems show that crustal permeability is created by dike  
630 emplacement. Geophysical data show major fracturing around dikes due to high magma pressure  
631 and wall-rock stress changes during dike emplacement (Roman and Cashman, 2006; Roman et al.,  
632 2006). Dike-related earthquakes manifest themselves geologically as damage zones of fracture  
633 systems along dike margins with marked increases in permeability (Farquharson et al., 2016).  
634 Complex fracturing and brecciation at dike jogs create porosity and permeability for fluid flow  
635 and alteration (e.g. Brown et al., 2007). In some eruptions, pathways for magmatic fluids to flow  
636 to the surface from deep in the magmatic system closely follow dikes supplying the volcano (e.g.  
637 Christopher et al., 2015). Based on observations of eruptions, geochronology, intrusive  
638 relationships, and thermal models, time scales of igneous activity range from 1 to  $<10^3$  years  
639 (Sheldrake et al., 2016). In contrast, periods of non-intrusion or volcanic repose are typically  $>10^3$   
640 to  $10^5$  years. Our observations at Don Manuel fit this pattern well. For DMIC dikes with widths of  
641 1 to 60 m, time scales of intrusion and solidification are in the range  $\sim 1$  to  $<10^2$  years while the  
642 time span of repetitive intrusion associated with mineralization is of order  $10^5$  years (Figure 15).  
643 Studies at other porphyry copper deposits (Cathles and Shannon, 2007; Mercer and Reed, 2013;  
644 Reed et al., 2013) have inferred rapid expulsion of ore-forming fluids occurred on time scales  
645 estimated at 20 to 900 years. Our observations, however, do not enable us to distinguish at DMIC  
646 between rapid pulses of fluid release triggered by individual episodes of dike emplacement and  
647 more continuous long-term release of fluids facilitated by the damaged regions created by multiple  
648 intrusions.

## **Role of mafic and silicic magmas in mineralization**

For DMIC, the early silicic intrusions, the quartz monzonite and rhyolite, were not mineralized. The onset of mineralization was associated with the mafic enclave-bearing biotite tonalite, reaching its peak with emplacement of the intermediate porphyry dikes, as indicated by high copper grades and abundance of Cu-Fe sulfides. These units associated with mineralization contain abundant hydrothermal biotite in addition to Cu-Fe sulfides indicating the presence of magmatic hydrothermal fluids. The hypabyssal intrusions themselves are far too small to provide the volumes of magmatic fluids necessary to form a porphyry copper deposit (e.g. Cline and Bodnar, 1991; Cloos, 2001; Sillitoe, 2010). These fluids must therefore derive from a much larger magmatic reservoir at depth (e.g. Yerington; Dilles and Einaudi, 1992; Dilles, 1987). We now discuss two models that have been developed to link the mineralizing fluids to the underlying magmatic system, placing observations at DMIC into context.

Many PCD models attribute mineralization to the release of a single magmatic fluid from a magma reservoir (Candela and Piccoli, 2005; Candela and Holland, 1984; Cline and Bodnar, 1991; Cloos, 2001; Cooke et al., 2014; Huber et al., 2012; Landtwing et al., 2005; Reed et al., 2013; Seedorff et al., 2005; Sillitoe, 2010; Weis et al., 2012). These models commonly postulate the steady release of fluids bearing Cu, Cl and S from a cooling and crystallizing silicic magma, along with interactions between the magmatic fluid and meteoric fluids. A single fluid model is not ruled out by our observations at DMIC, but the model does not explain the early period of barren silicic magmatism and the association of mineralization with mafic magma emplacement.

An alternative idea is that mafic magmas are the source of the S-rich, and in some models metal-rich, mineralizing magmatic fluids (Audetat and Pettke, 2006; Blundy et al., 2015; De Hoog et al., 2004; Halter et al., 2005; Hattori and Keith, 2001; Heinrich et al., 2005; Keith et al., 1997;

Maughan et al., 2002; Nadeau et al., 2010; Pollard et al., 2005; Sinclair, 2007; Zajacz and Halter, 2009). Blundy et al. (2015) developed this hypothesis further by invoking two different fluids: a Cl-rich and Cu-rich brine derived from silicic magma and a S-rich fluid sourced from the influx of mafic magma.

The early barren period of silicic magmatism at DMIC suggests early fluids lacked the right geochemistry for mineralization, consistent with release of Cl-rich but S-poor hydrous fluids. We cannot directly demonstrate that these fluids led to the accumulation of Cl and Cu-rich brines, as required by the two fluid hypothesis of Blundy et al. (2015), but the period of early barren silicic magmatism lasted ca. 200 kyr, providing time for discharge of hydrous fluids from the deeper silicic system that sourced the hypabyssal intrusions. This  $10^5$  yr timescale of silicic magma accumulation is directly comparable to the intrusive and antecrystic zircon record, well documented at other PCDs (Buret et al., 2016; Tapster et al., 2016).

An open question concerns the processes that could enable S-rich fluids derived from mafic magma to be involved in mineralization. Two possibilities have been discussed in the literature. Sulfur derived from degassing mafic magma could have been stored temporarily as anhydrite and then subsequently remobilized by breakdown of anhydrite in the shallow silicic magma reservoir as has been suggested for Yanacocha (Chambefort et al., 2008; Chambefort et al., 2013). Here the role of the mafic magma is to enrich the fluids within the silicic magma chamber in S leading to mineralization by a single fluid. In the model of Blundy et al (2015) however, metalliferous brine accumulates as proto-ore prior to injection of pulsed S-rich fluids derived from mafic magma injections. Our observations do not strongly favor one hypothesis over the other, but a prolonged period of barren silicic magmatism prior to mineralization and evidence for mafic recharge (Fig. 17) is anticipated in the latter hypothesis but not by the former.

## CONCLUSIONS

The DMIC units show magmatic complexity and chemical variation assembled in the upper crust in just over 400 kyr. The shallow-level intrusions within the DMIC represent short-lived injections of magma separated by periods of dormancy of 10s to 100s kyrs. The episodic emplacement and hybrid character of DMIC are features also found in arc volcanoes and other shallow intrusive complexes in arcs. These observations support the hypothesis that similar processes operate in the deeper portions of both arc volcanic and porphyry copper systems.

The DMIC evolved from barren silicic intrusions over about 100 kyrs to mineralized intrusions involving cogenetic mafic and silicic magmas. Based on petrographic and geochemical observations mingling and mixing between mafic and silicic magma occurred both in the deeper magma reservoir and during emplacement. These observations of the close association of mineralization with mafic magma intrusion are consistent with hypotheses of mafic magmas being a major source of sulfur.

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## FIGURE CAPTIONS

Figure 1. Location of the Don Manuel Igneous Complex (DMIC) study area, major volcanoes, and major porphyry copper deposits in central Chile.

Figure 2. (A) Geological map of the region around 34°S, including the locations of El Teniente porphyry copper deposit and Maipo volcano relative to the Don Manuel Igneous Complex (DMIC). (B) Inset shows the location of the Paredones and Don Manuel Principal areas within the study area. Map modified after Servicio Nacional de Geología y Minería (2002) and (Sruoga et al., 2005).

Figure 3. (A) Geological map of the Don Manuel area showing the surface geology, location of the Paredones and Don Manuel Principal sections of the study area, and the drill hole locations. Copper sulfides are confined to the Don Manuel Principal area. Map modified after (Candia et al., 2009). (B) Schematic geologic cross-section through the mineralized area at Don Manuel Principal. The cross-cutting relationships shown are dominantly based on logging by the lead author, supplemented by logs of surface samples and drill cores from BHP Billiton. Quartz monzonite dikes have intruded the Coya Machali Formation, followed by the emplacement of the equigranular phase of the biotite tonalite. A porphyritic phase of the biotite tonalite was emplaced after the equigranular phase of the biotite tonalite. A series of intermediate porphyry dikes cut the previous intrusions and are in turn cut by later basaltic andesite dikes.

1641 Figure 4. Don Manuel Igneous Complex (DMIC) units sampled from Don Manuel Principal core.  
1642 (A) Hornfelsed lacustrine sedimentary facies of the Coya Machali Formation showing a layer  
1643 replaced by chalcopyrite and calc-silicate minerals (core DM7, depth: 77.25 m); (B) Intermediate  
1644 porphyry with a chalcopyrite-quartz vein (core DM8, depth: 438.0 m); (C) Quartz monzonite (core  
1645 DM6, depth: 425.8 m); (D) Equigranular biotite tonalite with mafic enclaves (core DM2, depth:  
1646 107.9 m); (E) Porphyritic biotite tonalite (core DM4, depth: 472.4 m); (F) Intermediate porphyry  
1647 (core DM5, depth: 441.2 m); and (G) Basaltic andesite (core DM4, depth: 477.2 m). Abbreviation:  
1648 Ccp = chalcopyrite.

1649 Figure 5. Characteristic macroscopic textures of the intrusive units of the Don Manuel Igneous  
1650 Complex (DMIC) in the Don Manuel Principal drill core. The intermediate porphyry dikes may  
1651 show a much broader range of textures than shown here. (A) Quartz monzonite with biotite (core  
1652 DM6, depth: 120.6 m); (B) Porphyritic biotite tonalite containing both biotite and amphibole (core  
1653 DM4, depth: 472.4 m); (C) Equigranular biotite tonalite with only biotite in this particular sample  
1654 (core DM2, depth: 14.15 m); (D) Intermediate porphyry dike containing only biotite as  
1655 ferromagnesian phenocryst (IPD1) (core DM5, depth: 168.5 m); (E) Intermediate porphyry dike  
1656 containing both biotite and amphibole as ferromagnesian phenocrysts (IPD2) (core DM5, depth:  
1657 443.0 m); (F) Intermediate porphyry dike containing amphibole as the only ferromagnesian  
1658 phenocryst (IPD3) (core DM6, depth: 465.3 m); (G) Basaltic andesite dike with amphibole  
1659 phenocrysts (core DM6, depth: 534.8 m). Abbreviations: Bt = biotite, Ksp = potassium feldspar,  
1660 Am = amphibole, Pl = plagioclase, Py = pyrite, Qtz = quartz.

1661 Figure 6. Photomicrographs of the Don Manuel Igneous Complex (DMIC) units in the drill core  
1662 from Don Manuel Principal showing (A) Quartz monzonite with plagioclase phenocrysts; cross-  
1663 polarized light (core DM6, depth: 120.6 m); (B) Biotite tonalite with plagioclase, quartz and

1664 biotite; cross-polarized light (core DM4, depth: 285.3 m); (C) Intermediate porphyry dike with  
1665 plagioclase and amphibole phenocrysts; cross-polarized light (core DM6, depth: 527.8 m); (D)  
1666 Mirolitic cavity filled with quartz, pyrite and epidote; cross-polarized light (core DM3, depth:  
1667 563.0 m); (E) Basaltic andesite dike, with plagioclase and amphibole phenocrysts; cross-polarized  
1668 light (core DM5, depth: 503.0 m); (F) Contact between intermediate porphyry dike and basaltic  
1669 andesite with plagioclase phenocryst; cross-polarized light (core DM6, depth: 546.0 m).  
1670 Photomicrographs of DMIC units from the Paredones area showing (G) Rhyolite with plagioclase  
1671 phenocrysts in a finer groundmass of quartz, plagioclase and potassium feldspar; cross-polarized  
1672 light (sample location: 34°13'55.2"S, 70°4'48"W); (H) Basaltic andesite dike with clinopyroxene  
1673 phenocryst; cross-polarized light (sample location: 34°13'44.4"S, 70°5'2.4"W); Abbreviations: Bt  
1674 = biotite, Ep = epidote, Am = amphibole, Cpx = clinopyroxene, Pl = plagioclase, Py = pyrite, Qtz  
1675 = quartz.

1676 Figure 7. Representative textural relationships within the intermediate porphyry dikes of the Don  
1677 Manuel Igneous Complex (DMIC): (A) Enclaves within an intermediate porphyry dike (core DM3,  
1678 depth: 298.0 m); (B) Intermediate porphyry dike showing flow zones, diffuse contacts between  
1679 magma pulses, and microenclaves (core DM3, depth: 168.1 m). Flow zones suggest magma mixing  
1680 produced this hybridized texture.

1681 Figure 8. Irregular contact between the rhyolite (bottom) and a basaltic andesite dike (top) in  
1682 outcrop in the Paredones region of the study area.

1683 Figure 9. Total alkalis vs silica (TAS) diagram after Le Maitre et al. (2002) of the Don Manuel  
1684 Igneous Complex (DMIC) whole rock samples. DMIC samples range from basaltic andesites  
1685 through to rhyolites (anhydrous normalized).

1686 Figure 10. Selected major element vs. SiO<sub>2</sub> Harker diagrams for the Don Manuel Igneous Complex  
1687 (DMIC). Total Fe is plotted as FeO\*. Symbols are the same as in Figure 9.

1688 Figure 11. Whole-rock REE concentrations normalized to average chondrite (Sun and  
1689 McDonough, 1989) for the rocks of the Don Manuel Igneous Complex (DMIC).

1690 Figure 12. Plots of (A) Sr/Y vs. Y and (B) La/Yb vs. Yb for the rocks of the Don Manuel Igneous  
1691 Complex (DMIC). Fields for adakites and normal arc trends are after Defant and Drummond  
1692 (1993) and (Castillo, 2012). Symbols are the same as in Figure 9.

1693 Figure 13. Typical zoning profiles from core to rim of anorthite content (mol. %) in plagioclase  
1694 phenocrysts from the rhyolite and basaltic andesite dikes from the Paredones area. White arrows  
1695 mark the line of each traverse. Anorthite zoning is mostly absent in the rhyolite and is characterized  
1696 by a slow decay towards the rim in the basaltic andesite.

1697 Figure 14. Typical zoning profiles from core to rim of anorthite content (mol. %) in plagioclase  
1698 phenocrysts from the intermediate porphyry dikes from Don Manuel Principal drill core. All  
1699 phenocryst types can be found in the same sample. Arrows mark the line of each traverse.

1700 Figure 15. CA-ID-TIMS <sup>206</sup>Pb/<sup>238</sup>U fraction dates (corrected for initial <sup>238</sup>U–<sup>230</sup>Th disequilibrium  
1701 with Th/U<sub>magma</sub> ~ 3.5, see DR3) and weighted mean dates for each unit of the Don Manuel Igneous  
1702 Complex (DMIC). Weighted mean dates are interpreted as emplacement ages. All uncertainties  
1703 are shown at the 2σ confidence level.

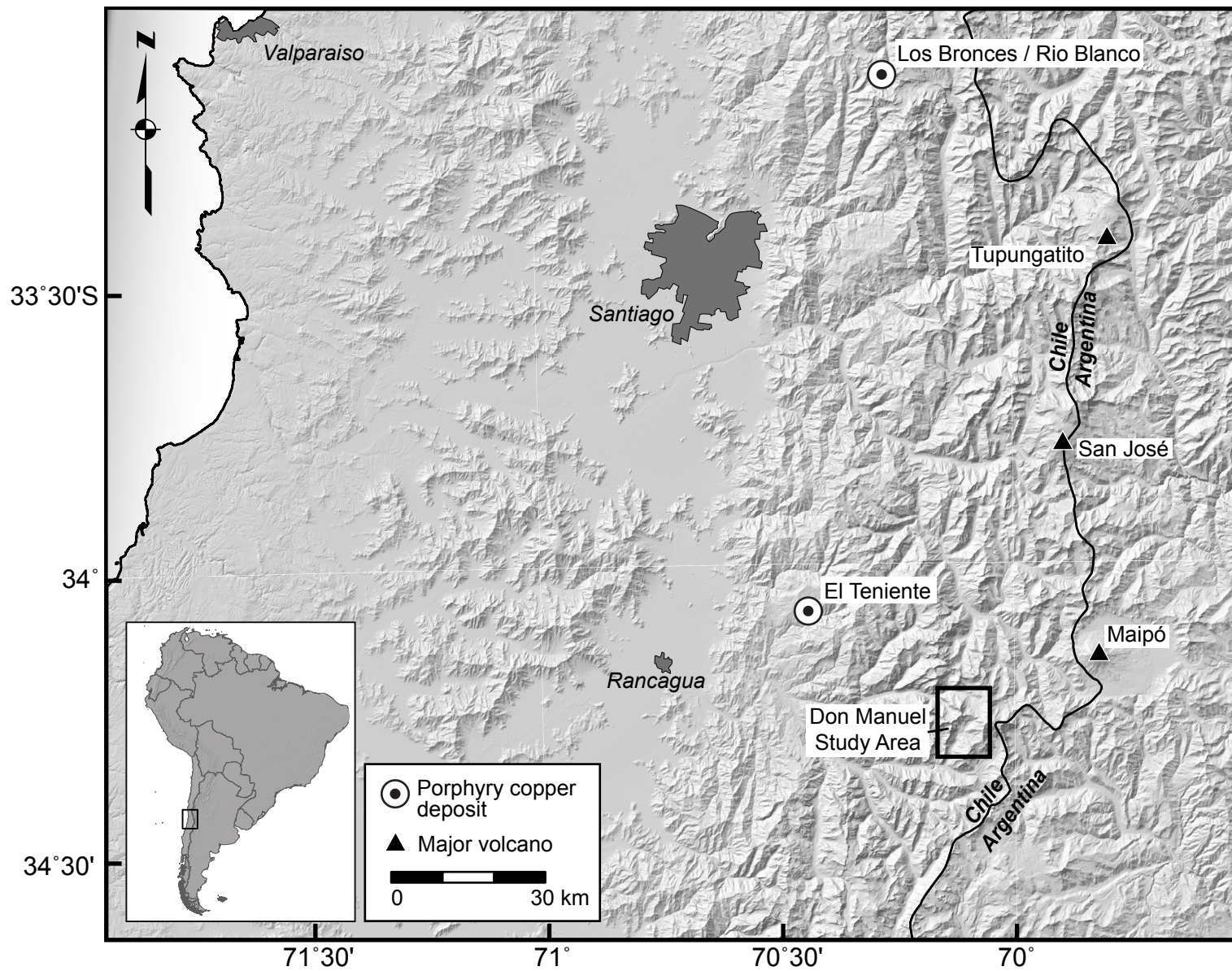
1704 Figure 16. Whole rock argon data for the Don Manuel Igneous Complex (DMIC) basaltic andesite  
1705 dikes (see Table 4). <sup>40</sup>Ar/<sup>39</sup>Ar step-heating plateau diagrams including %<sup>40</sup>Ar\*, K/Ca and age vs.  
1706 %<sup>39</sup>Ar released per step are shown on the left. The inverse isochron analysis on the right shows an

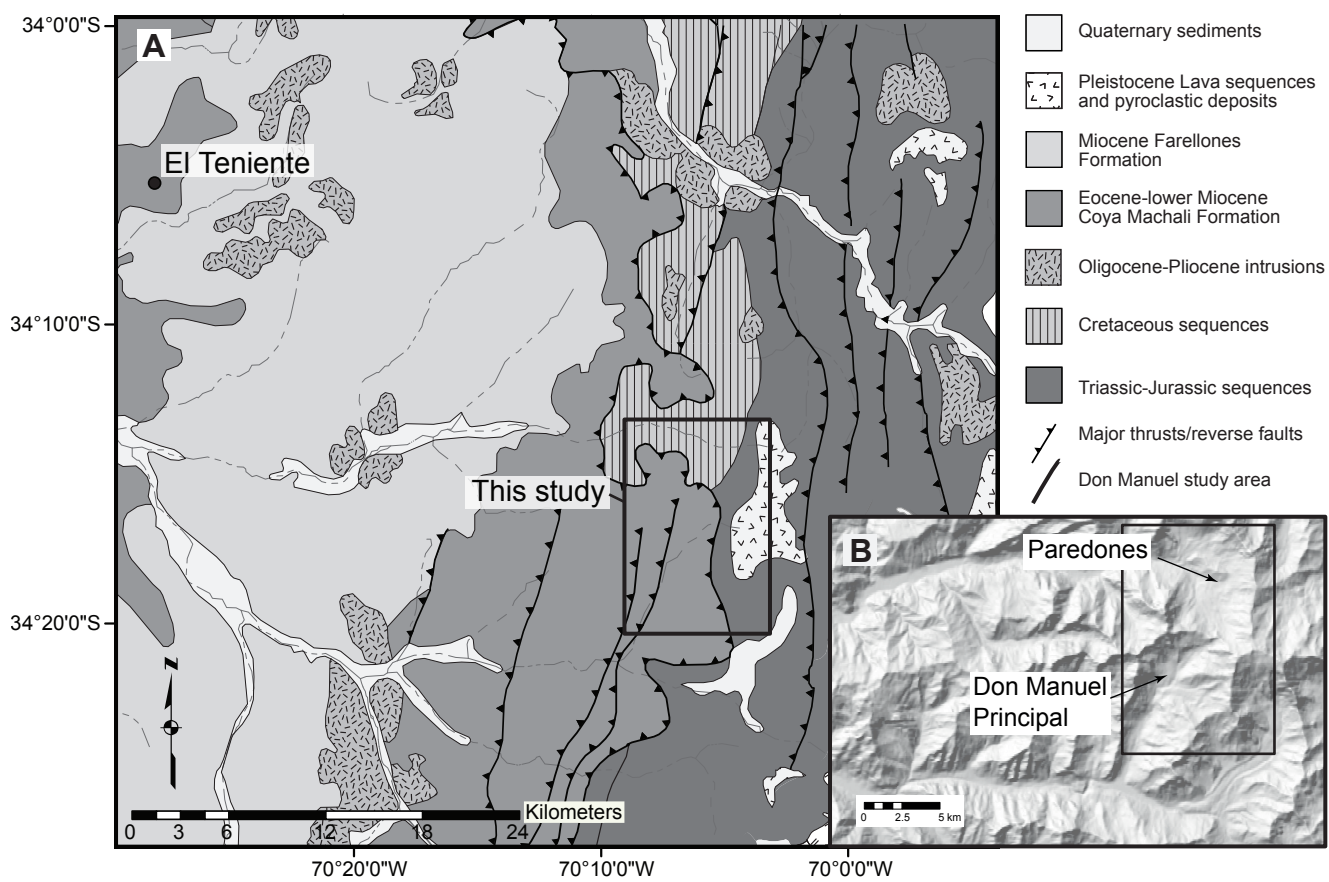
1707 age and composition of the trapped component for a number of points (n). The ages presented in  
1708 the plateau diagram (left panel) are calculated using air as a trapped component.

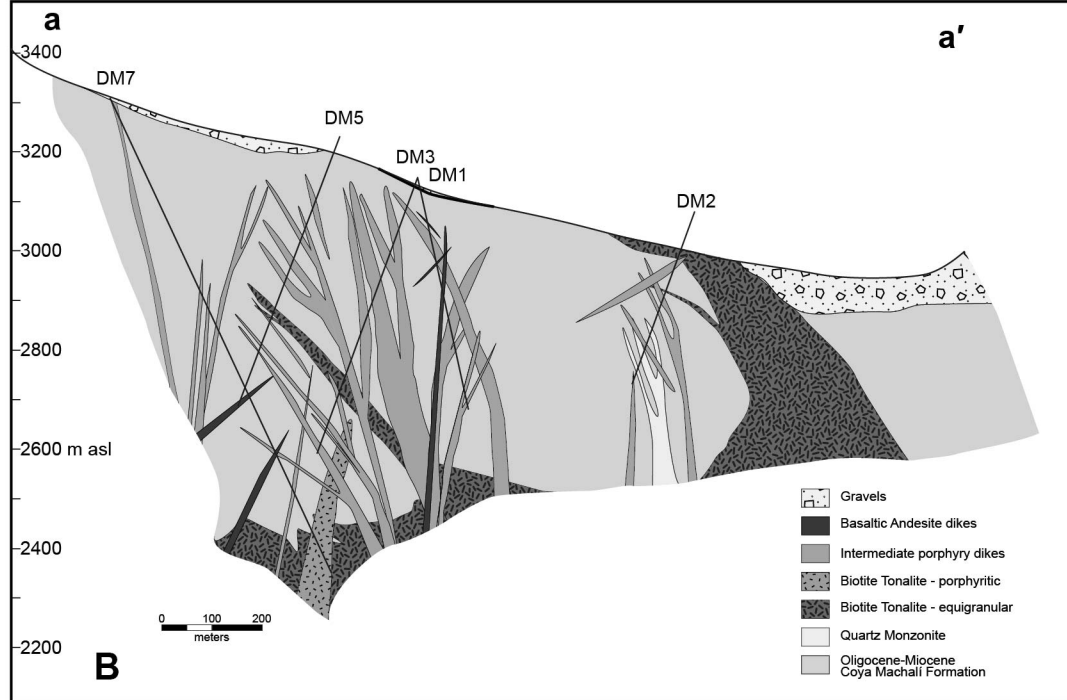
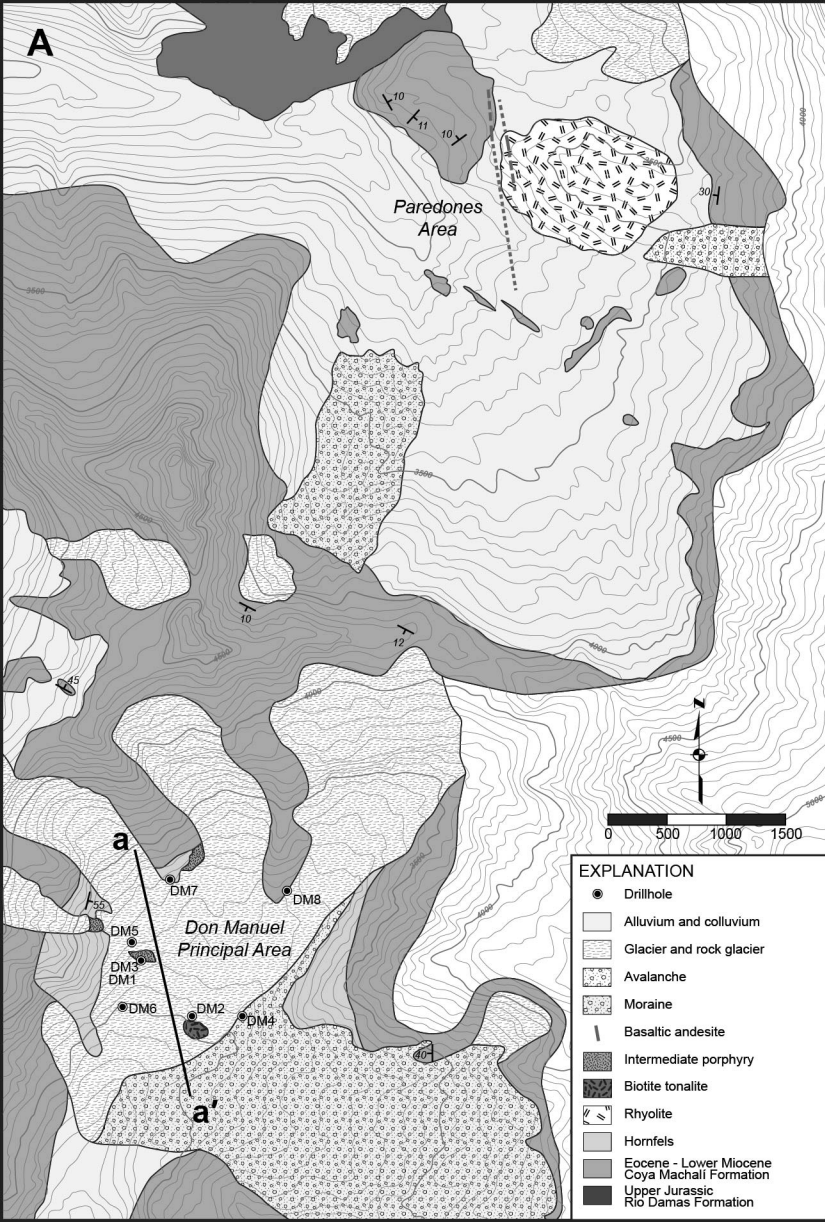
1709 Figure 17. Summary of the Don Manuel Igneous Complex (DMIC) emplacement events including  
1710 CA-ID-TIMS U-Pb zircon dates (circles), whole-rock  $^{40}\text{Ar}/^{39}\text{Ar}$  dates (squares), and observed  
1711 mafic enclaves within dated units (triangles). Gray filled circles indicate strongly mineralized  
1712 units. Data are given in Figure 15, Figure 16 and Table 3 and Table 4. IPD, intermediate porphyry  
1713 dike.

1714 <sup>1</sup>GSA Data Repository items 2016xxx, analytical methods and additional analytical results are  
1715 available online at [www.geosociety.org/pubs/ft20XX.htm](http://www.geosociety.org/pubs/ft20XX.htm), or on request from  
1716 [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301,  
1717 USA.

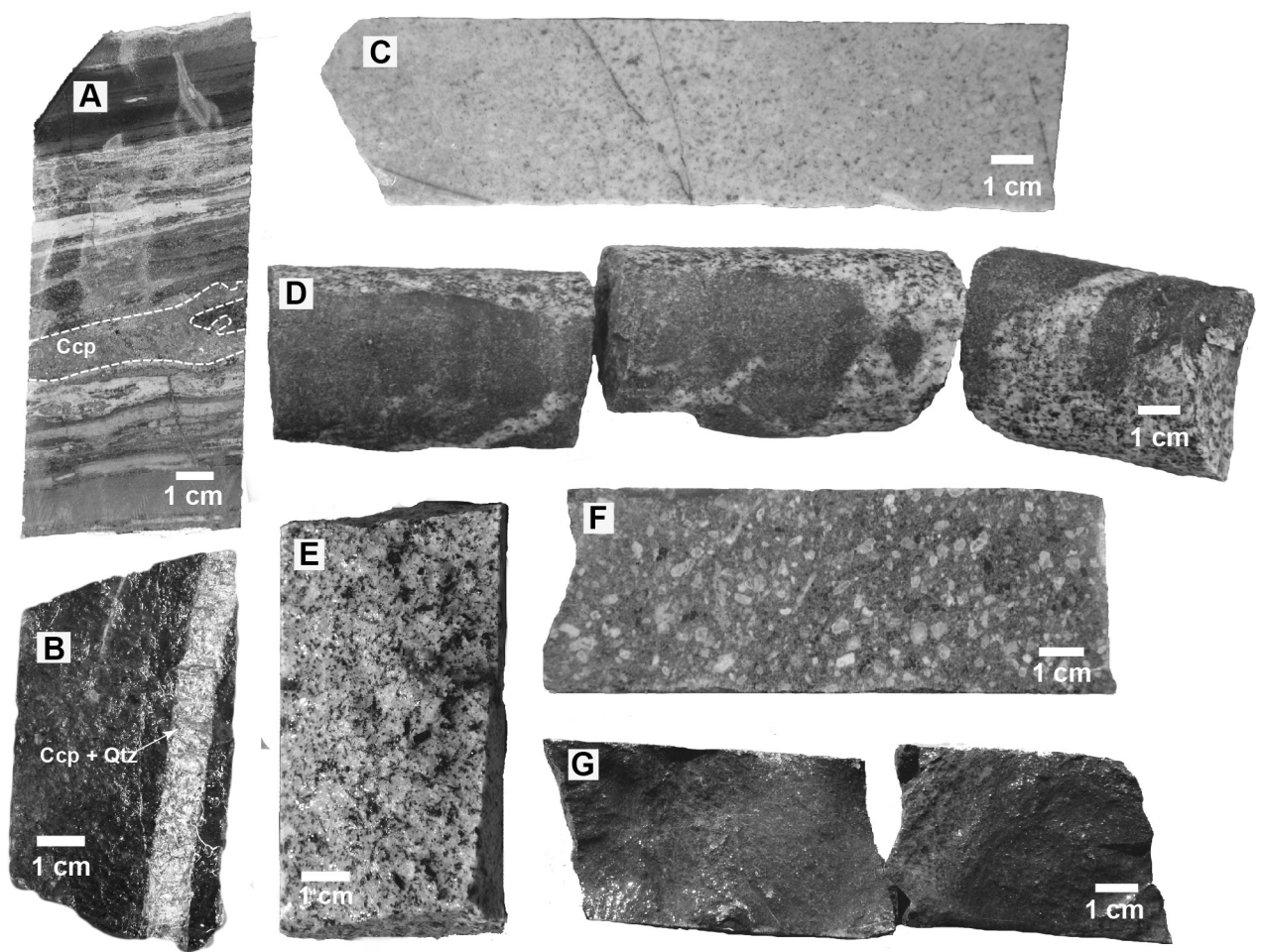


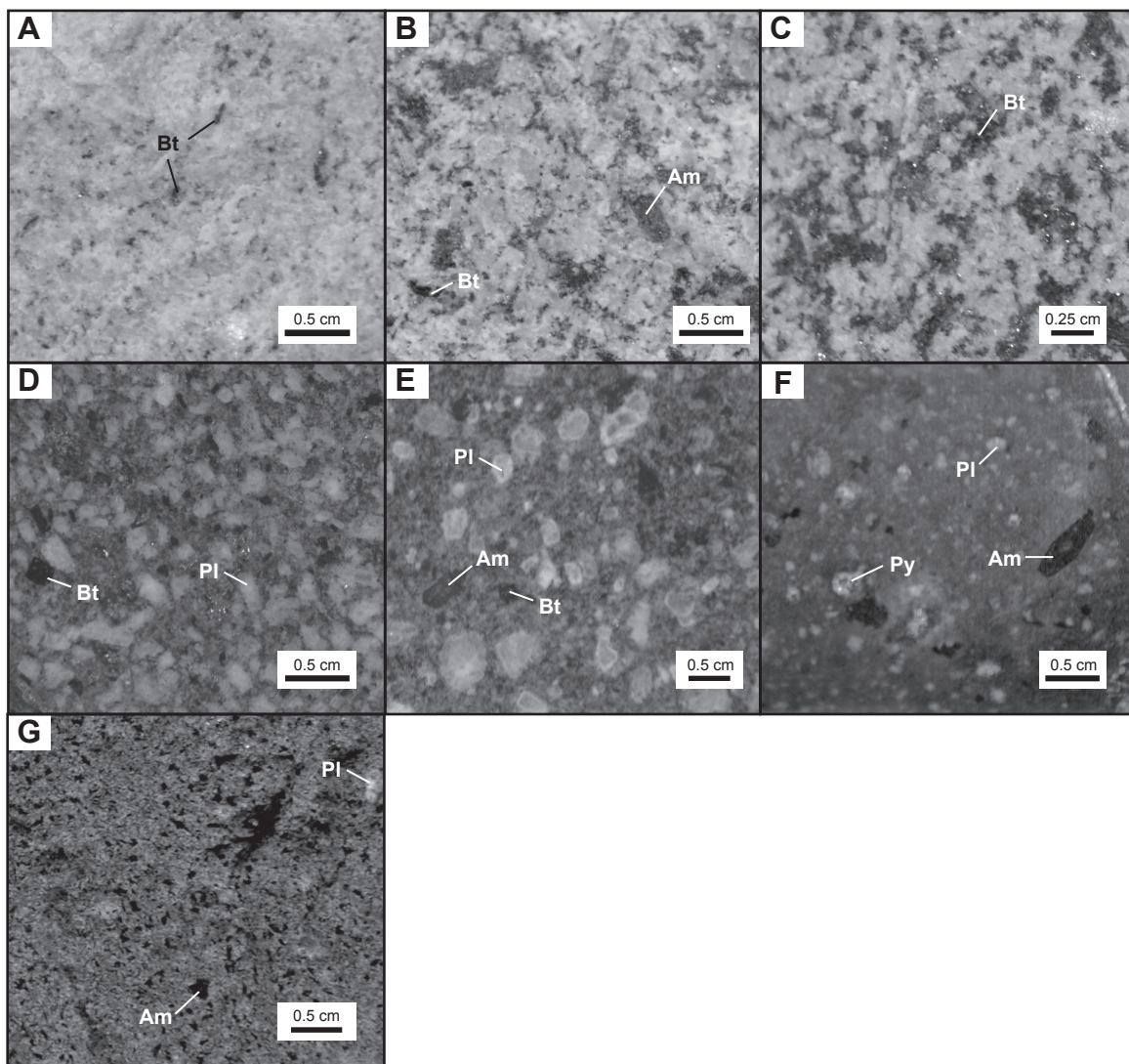




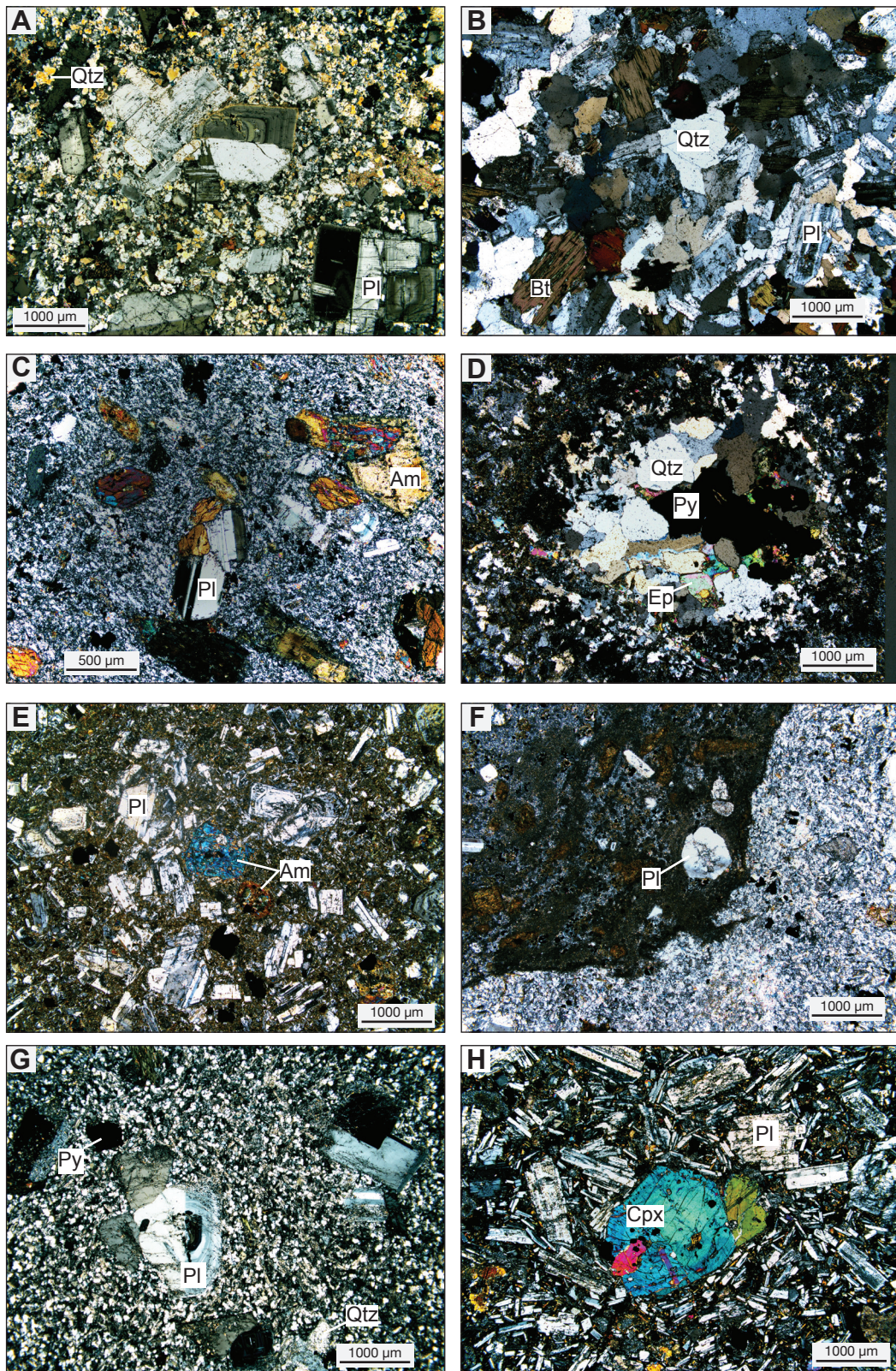










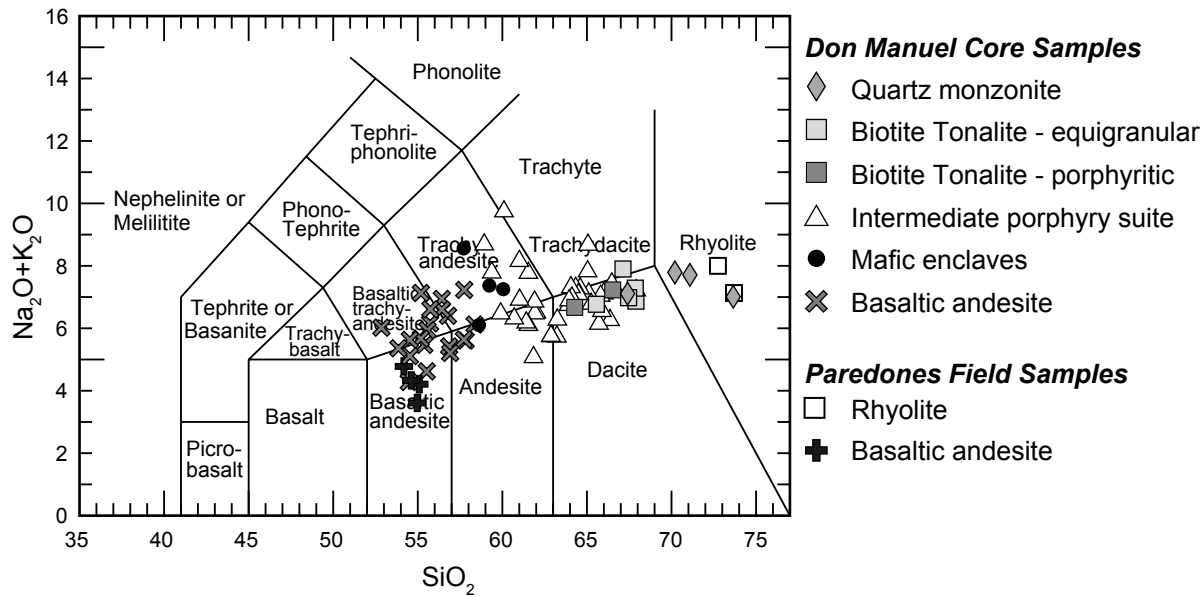




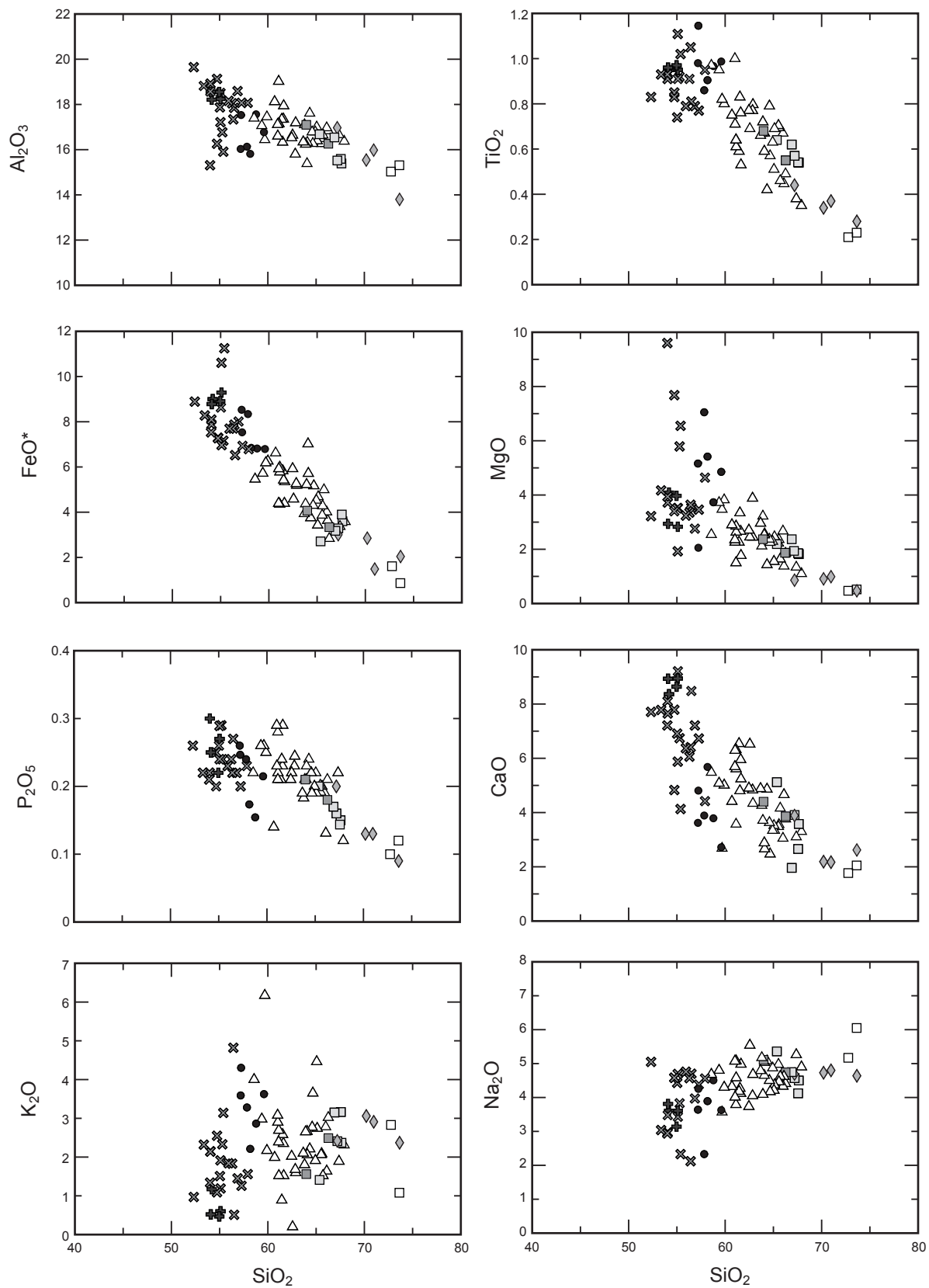




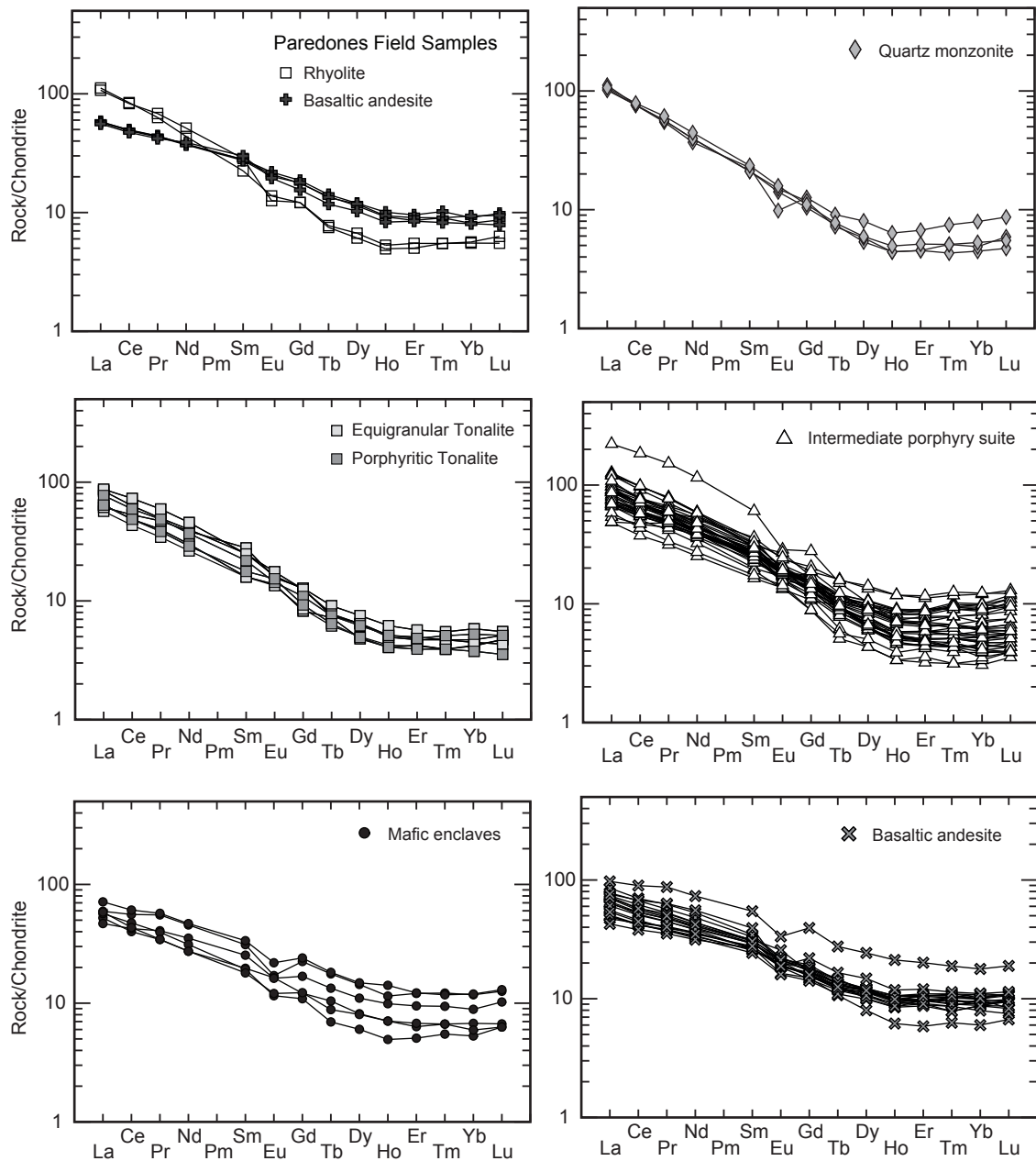




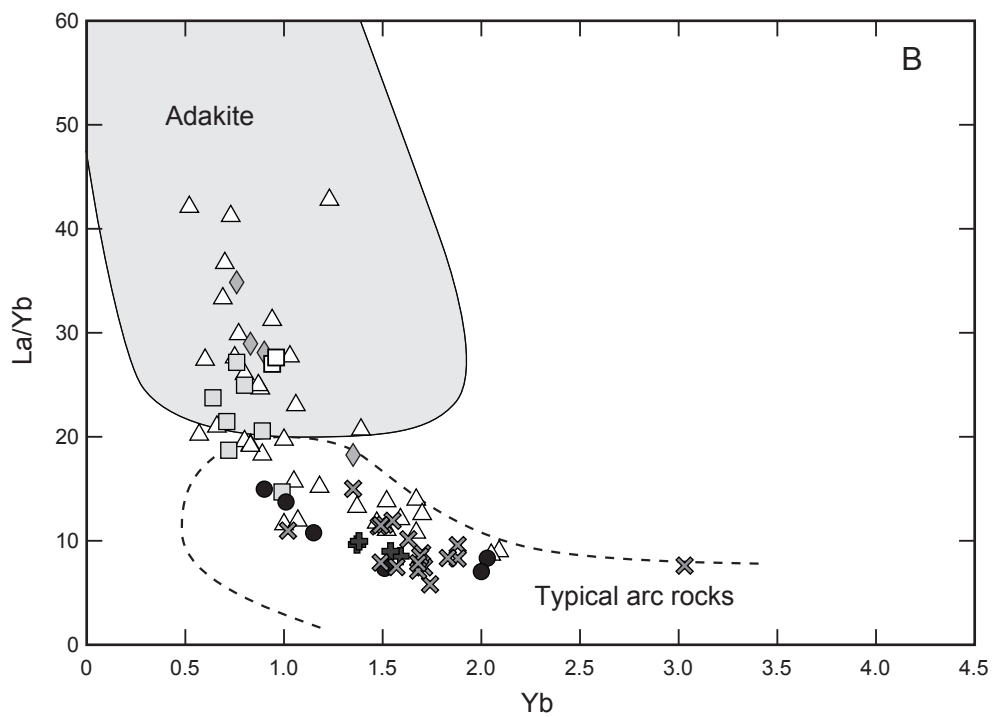
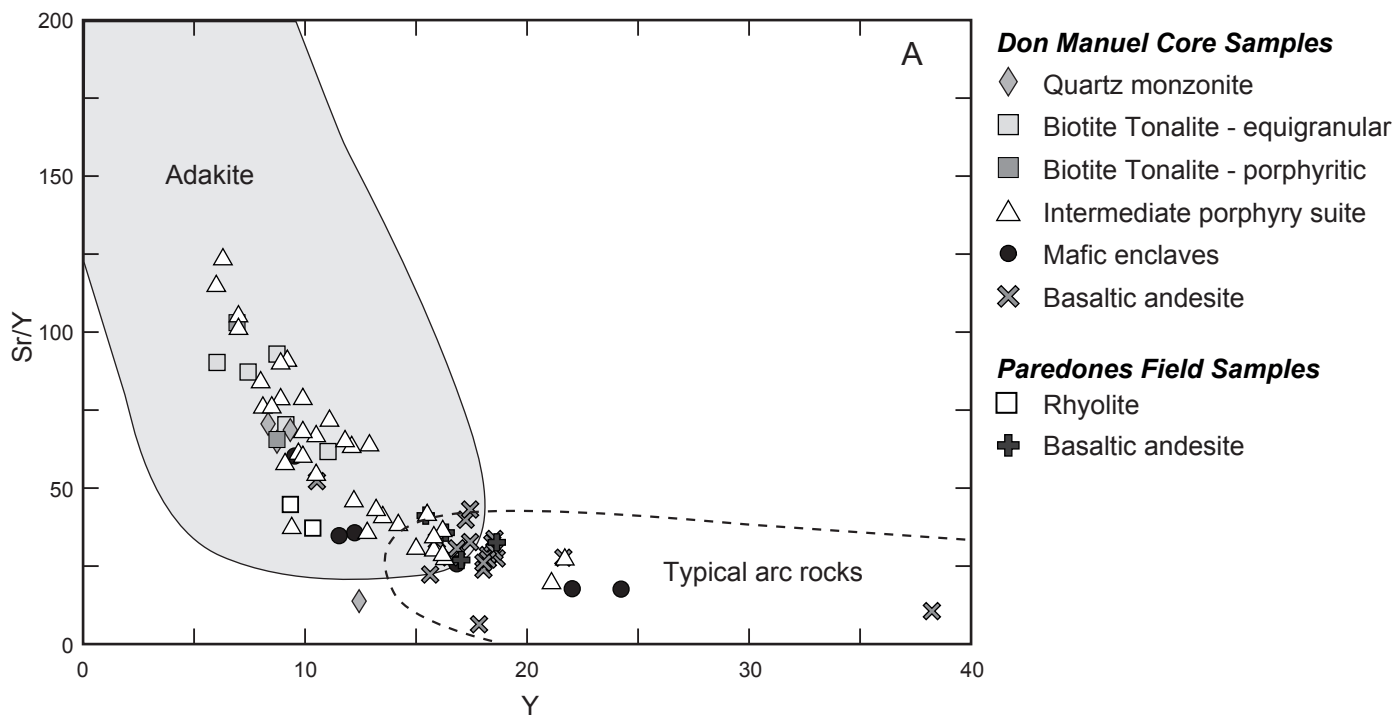
Gilmer, Figure 9, B31524

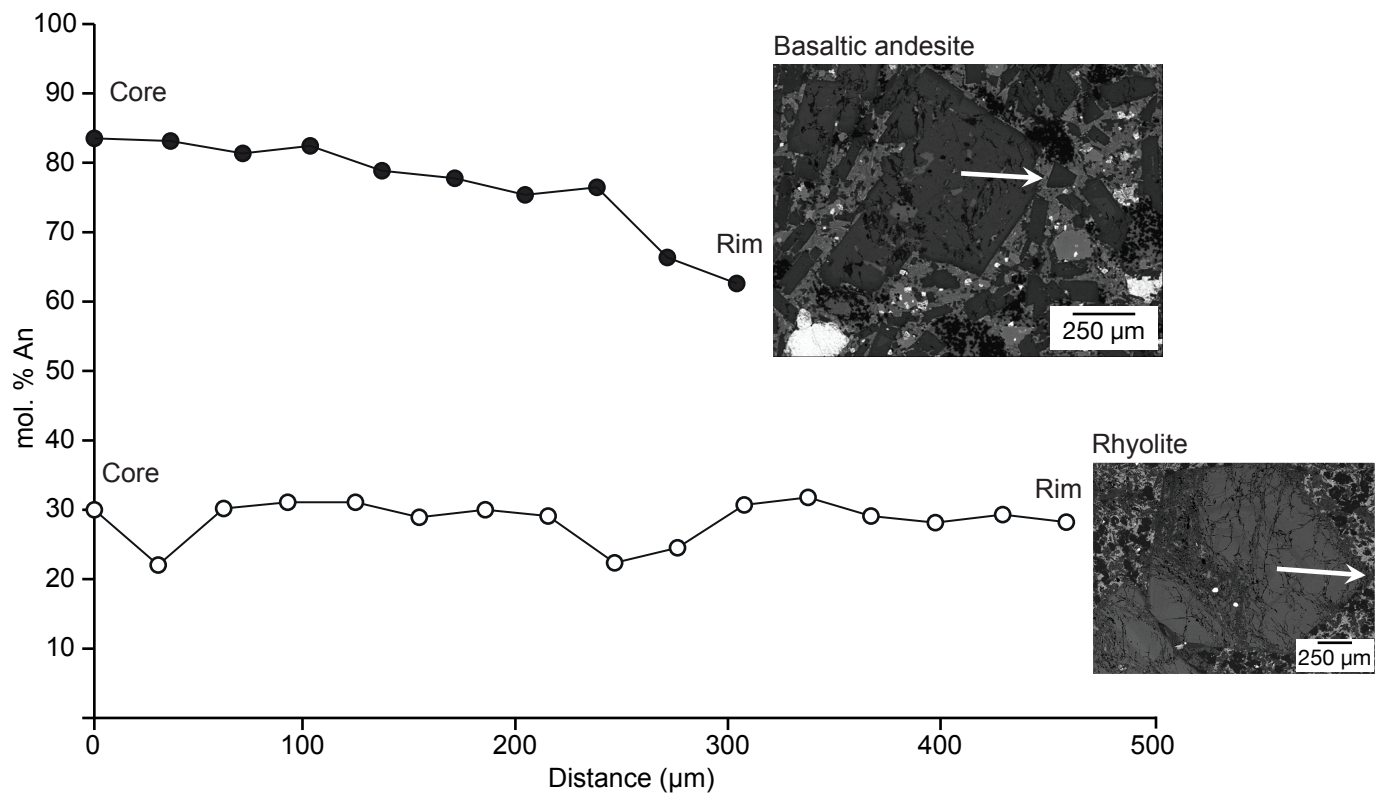


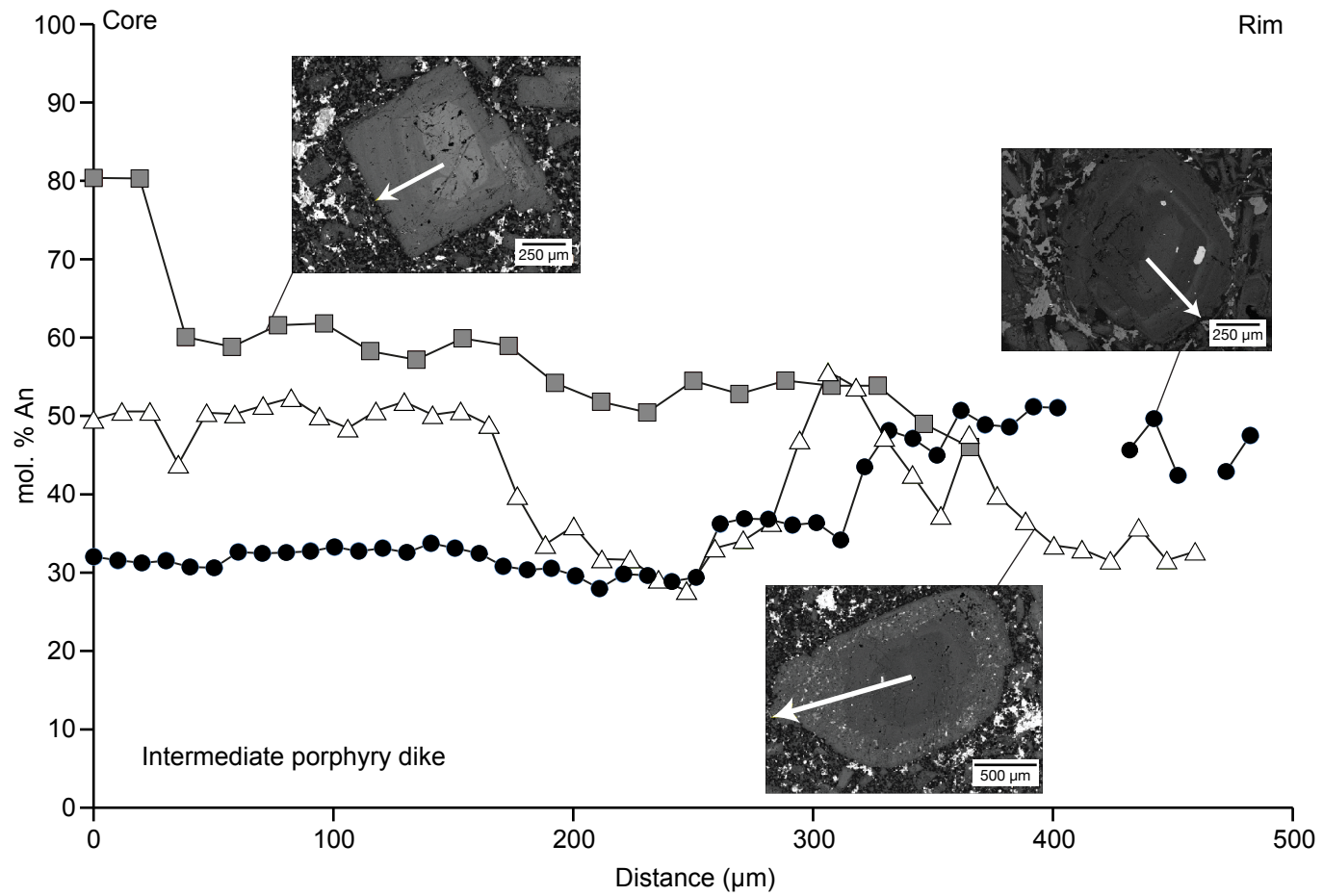
Gilmer, Figure 10, B31524

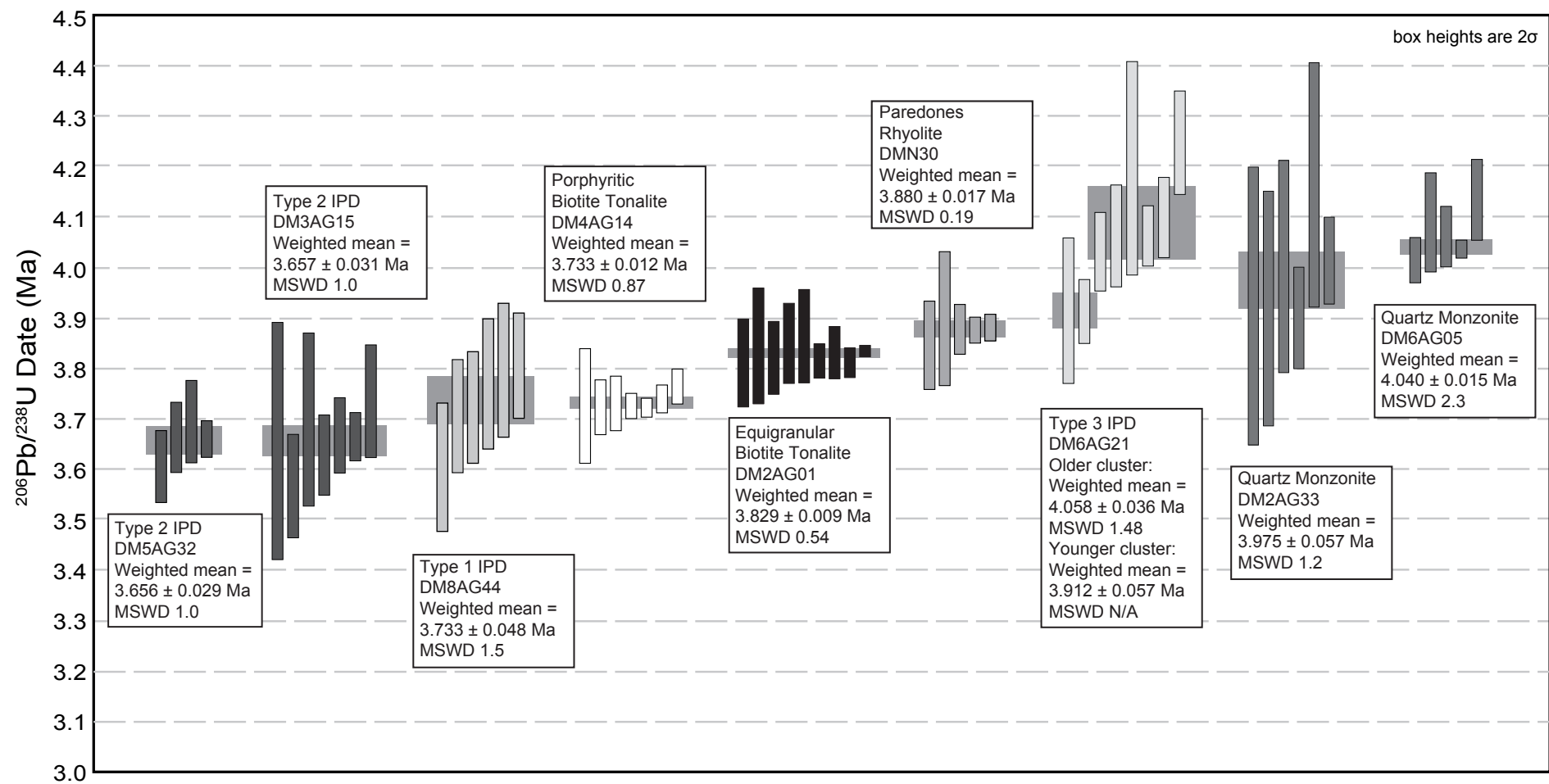


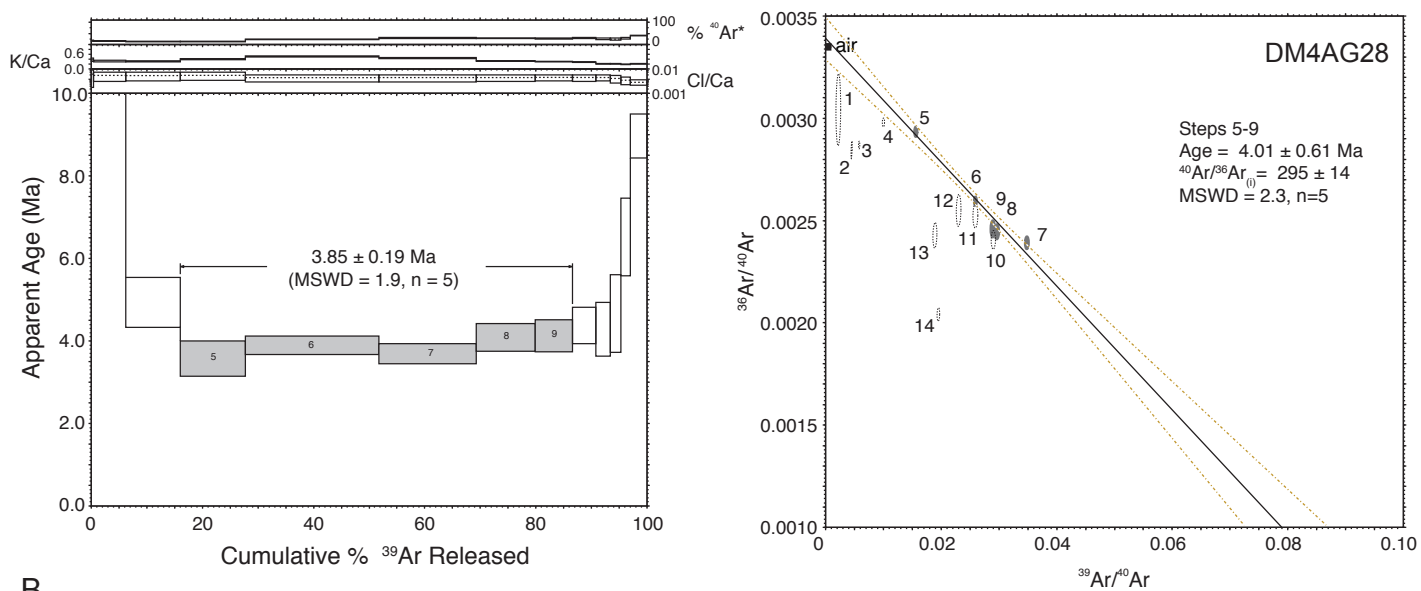
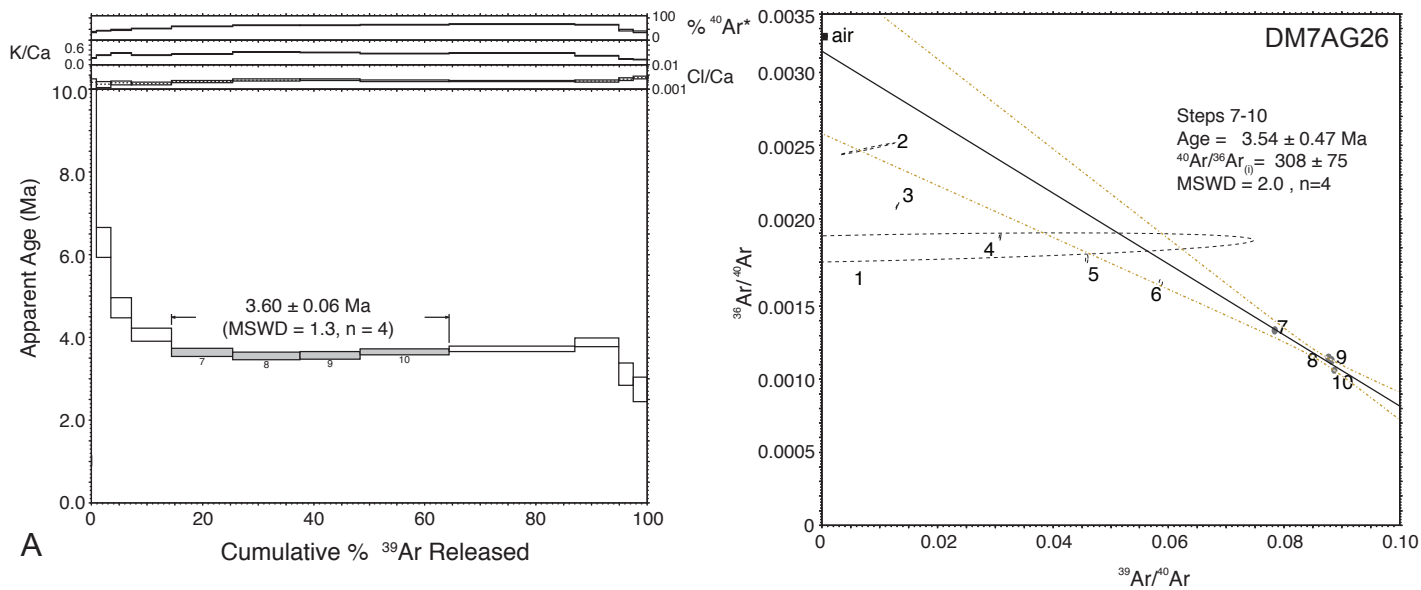
Gilmer, Figure 11, B31524



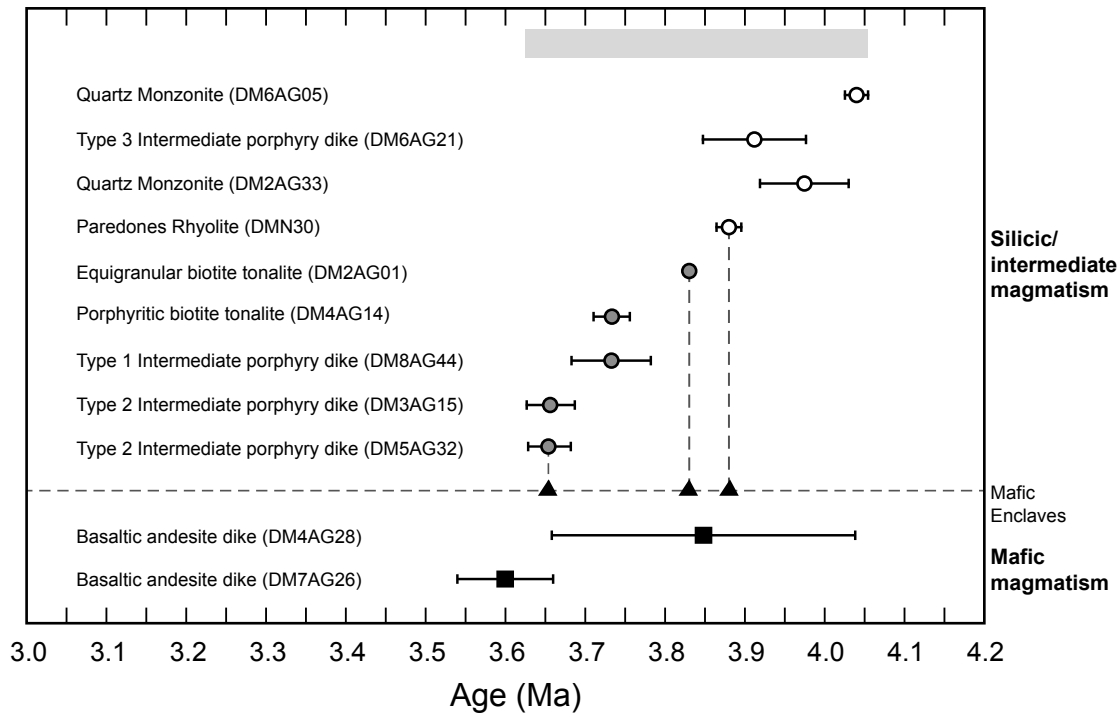
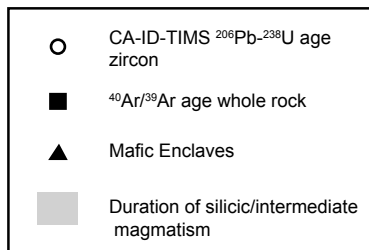












Gilmer, Figure 17, B31524

TABLE 1. REPRESENTATIVE BULK ROCK CHEMICAL ANALYSES OF THE DON MANUEL IGNEOUS COMPLEX

	Don Manuel Principal units													Paredones units			
Sample	DM2AG33	DM6AG05	DM2AG01	DM4AG14	DM5AG13	DM6AG11	DM6AG21	DM8AG53	DM2AG47	DM1AG10	DM5AG07	DM6AG17	DM8AG40	DMN30	DMN36	DMN16	DMN17
Rock Type	QM	QM	BT	BT	IPD	IPD	IPD	IPD	ME	ME	BA	BA	BA	PR	PR	PBA	PBA
SiO <sub>2</sub>	68.79	69.79	67.33	62.95	63.18	59.77	61.71	60.38	54.49	55.89	55.23	54.02	51.38	71.7	71.57	52.52	51.31
TiO <sub>2</sub>	0.34	0.36	0.54	0.67	0.56	0.8	0.68	0.58	1.09	0.83	0.92	0.82	0.82	0.21	0.22	0.92	0.9
Al <sub>2</sub> O <sub>3</sub>	15.22	15.71	15.54	16.82	15.9	15.86	16.41	17.04	16.69	15.59	17.75	18.89	19.3	14.81	14.88	17.73	17.24
Fe <sub>2</sub> O <sub>3</sub> *	0.99	N.D.	1.06	N.D.	N.D.	1.38	N.D.	N.D.	N.D.	N.D.	1.86	N.D.	N.D.	0.37	N.D.	N.D.	2.48
FeO	1.90	1.46	2.93	4.00	5.05	4.02	4.51	5.73	7.17	8.06	5.97	7.18	8.73	1.25	0.84	8.52	6.29
MnO	0.05	0.03	0.03	0.06	0.02	0.06	0.1	0.07	0.06	0.05	0.14	0.11	0.1	0.07	0.06	0.16	0.17
MgO	0.89	0.98	1.85	2.34	2.2	3.24	2.41	2.22	1.96	6.81	3.37	3.36	3.16	0.46	0.5	3.8	3.88
CaO	2.15	2.13	2.65	4.33	2.41	4.66	6.43	6.43	4.58	3.76	6.03	7.69	7.57	1.74	1.99	8.26	7.91
Na <sub>2</sub> O	4.64	4.72	4.11	5.03	4.07	4.15	5.46	4.11	4.05	2.25	4.61	4.52	4.96	5.09	5.89	3.01	3.41
K <sub>2</sub> O	3.00	2.87	3.15	1.53	3.56	2.51	0.19	0.87	4.1	3.17	1.78	1.08	0.96	2.79	1.05	0.45	1.11
P <sub>2</sub> O <sub>5</sub>	0.13	0.13	0.14	0.21	0.18	0.24	0.21	0.21	0.23	0.24	0.25	0.25	0.26	0.1	0.12	0.21	0.24
LOI <sup>†</sup>	1.32	0.95	1.16	0.57	2.43	2.31	2.06	0.56	3.86	1.9	1.61	1.48	0.52	0.99	2.43	3.1	4.03
Total	99.41	99.13	100.49	98.51	99.58	98.99	100.2	98.2	98.29	98.55	99.51	99.4	97.75	99.57	99.54	98.67	98.98
S <sup>§</sup>	<0.02	0.54	0.58	<0.02	2.88	0.83	1.61	0.02	2.98	1.79	<0.02	1.24	<0.02	<0.02	<0.02	<0.02	<0.02
Sc	2.40	3.10	6.80	8.30	7.1	9.8	8.1	10.5	19.5	16.6	17.1	15.7	13.8	2.6	2.2	18.1	18.4
V	38.80	52.70	80.70	111.20	98.7	126	117.5	120.1	188.8	160.2	198.8	185.5	177.5	18.8	25.3	204.2	201.1
Cr	10.60	6.60	35.40	35.80	41.8	85.8	31.6	29.8	83.5	303.2	6.3	6.7	6.4	8.6	11.5	13.4	13.5
Co	5.70	3.50	10.60	10.00	21.7	11.8	8.2	9.7	34.2	11.9	12.5	10.4	18.1	2.8	1.2	23.1	23
Ni	16.60	4.50	15.20	15.80	13.8	22.4	55.1	25.4	46.9	113.3	13.6	7.7	17.2	16.4	2.9	69.9	15.1
Zn	48.20	10.10	24.80	39.00	12.8	25.8	37.5	67.9	44.2	35.4	45.7	37.2	62.8	24.8	6.9	85.3	73.9
Ga	20.10	16.50	19.50	17.60	18.9	19.9	17.7	17.2	19.7	19.8	15.9	19.2	25.8	19.7	18.8	19.4	17.8
Rb	70.20	56.90	144.50	46.70	120.1	93.8	5	45.3	117.5	210.2	77.2	46.6	48.9	67.7	30.9	7.6	19.8
Sr	565.00	586.90	542.30	711.60	688.4	794.3	766.8	586.3	429.3	573.8	551.4	625.5	600.4	436.9	394.7	608.8	460.2
Y	8.70	8.30	6.00	6.90	6	11.1	11.8	16.2	24.2	9.5	18.5	18.5	21.6	9.3	10.6	18.6	17
Zr	178.70	124.80	183.00	101.80	127.1	133.6	124.6	101.4	172.9	115.4	79.5	81.6	81.9	126.4	125.9	92.3	83.4
Nb	4.32	5.10	3.92	3.25	4.27	5.26	4.37	3.06	4.47	4.33	2.7	2.68	3.34	5.65	5.32	2.91	2.53
Sn	6.78	0.15	1.44	0.95	1.19	1.34	1.1	1.06	1.48	5.13	1.12	1.35	2.02	4.14	0.7	4.54	3.45

Cs	2.98	1.18	5.17	2.44	3.11	4.37	0.33	3.29	3.43	12.94	6.83	1.63	5.01	1.16	2.93	0.51	0.7
Ba	750.80	908.80	678.20	502.00	965.1	574.9	203.3	161.2	611.4	297.6	281.5	273.5	155.8	756.6	253.1	258.1	248.7
La	24.03	26.49	15.24	15.20	21.89	21.68	12.77	17.99	16.91	13.47	15.61	14.37	18.02	26.52	25.39	13.84	13.55
Ce	46.53	46.62	29.75	29.78	43.07	45.84	28.65	35.67	37.24	29.05	32.7	30.97	41.29	51.59	50.63	30.22	29.87
Pr	5.38	5.35	3.80	3.65	5.33	6.1	4.16	4.7	5.43	3.76	4.48	4.23	6.01	6	6.48	4.18	4.12
Nd	18.52	18.57	14.03	13.50	20.44	24.29	17.78	18.7	21.86	14.57	18.94	18.02	25.94	20.42	24	17.64	17.34
Sm	3.22	3.24	2.44	2.71	3.86	4.96	4.05	4.1	5.14	2.95	4.82	4.49	6.02	3.43	4.36	4.28	4.2
Eu	0.87	0.82	0.80	0.89	0.94	1.17	1.11	1.1	1.27	0.67	1.49	1.23	1.09	0.8	0.73	1.27	1.17
Gd	2.43	2.14	1.69	1.90	2.28	3.03	2.88	3.15	4.94	2.24	3.45	3.51	4.51	2.49	2.5	3.83	3.65
Tb	0.27	0.28	0.27	0.24	0.23	0.37	0.37	0.44	0.68	0.26	0.5	0.51	0.62	0.28	0.29	0.53	0.5
Dy	1.47	1.36	1.22	1.25	1.1	1.97	2.08	2.71	3.77	1.53	2.99	3.08	3.76	1.55	1.7	3.04	3
Ho	0.25	0.25	0.23	0.23	0.19	0.33	0.38	0.51	0.8	0.28	0.59	0.6	0.67	0.28	0.3	0.57	0.53
Er	0.75	0.75	0.70	0.65	0.53	0.97	1.06	1.47	2.02	0.84	1.73	1.77	1.99	0.83	0.91	1.58	1.5
Tm	0.13	0.11	0.10	0.10	0.08	0.15	0.17	0.24	0.3	0.14	0.26	0.27	0.29	0.14	0.14	0.26	0.23
Yb	0.83	0.76	0.71	0.64	0.52	0.88	1.07	1.67	2.03	0.9	1.88	1.69	1.88	0.96	0.94	1.54	1.59
Lu	0.15	0.12	0.12	0.09	0.09	0.13	0.17	0.24	0.33	0.16	0.27	0.28	0.29	0.16	0.14	0.25	0.24
Hf	4.28	3.27	4.21	2.61	3.3	3.47	3.14	2.66	4.43	3.05	2.18	2.22	2.24	3.46	3.27	2.59	2.34
Ta	0.37	0.37	0.35	0.26	0.3	0.35	0.28	0.19	0.33	0.28	0.16	0.16	0.17	0.44	0.41	0.17	0.18
Pb	19.72	9.03	6.68	5.16	4.91	5.73	5.65	4.05	6.25	2.92	2.69	2.15	3.96	16.97	5.22	5.13	5.31
Th	11.42	5.34	6.66	4.35	5.29	5.06	3.94	2.64	4.21	5.6	1.81	1.86	2.02	8.16	5.65	3.44	2.67
U	2.31	1.60	1.86	1.07	1.52	1.58	1.22	0.72	1.72	2.88	0.61	0.49	1.27	2.18	1.68	0.62	0.61

*Note:* QM—quartz monzonite; BT-biotite tonalite; IPD-intermediate porphyry dike; ME-mafic enclave; BA-basaltic andesite; PR-Paredones rhyodacite; PBA-Paredones basaltic andesite. Units in wt%.

\*Fe<sup>2+</sup>/Fe<sup>3+</sup> by iron titration analysis at Acme Analytical Laboratories Ltd., Canada. †LOI—loss on ignition. §Sulfur analyzed separately at Acme Analytical Laboratories Ltd., Canada.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF PLAGIOCLASE PHENOCRYSTS AND MICROPHENOCRYSTS

Sample	DM1AG31	DM1AG31	DM8AG53	DM8AG53	DM6AG11	DM6AG11	DM3AG38	DM3AG38	DMN30	DMN30	DMN16	DMN16	DM6AG05	DM6AG05	DM2AG23	DM2AG23	DM5AG34
Host	IPD	IPD	IPD	IPD	IPD	IPD	ME	ME	PR	PR	PBA	PBA	QM	QM	BT	BT	BA
	pheno.	micro-pheno.	pheno.	micro-pheno.	pheno.	micro-pheno.	micro-pheno.	micro-pheno.	pheno.	micro-pheno.	pheno.	micro-pheno.	pheno.	micro-pheno.	pheno.	micro-pheno.	pheno.
SiO <sub>2</sub>	52.53	53.37	49.90	54.89	54.70	54.57	48.54	56.53	60.95	62.96	46.30	46.50	60.74	65.96	60.38	59.42	49.12
TiO <sub>2</sub>	0.02	0.02	0.02	0.03	0.03	0.02	bdl	bdl	bdl	bdl	0.02	0.02	bdl	bdl	bdl	0.01	0.03
Al <sub>2</sub> O <sub>3</sub>	29.74	28.86	31.92	27.93	27.64	27.85	32.57	27.61	24.97	23.38	33.26	32.68	24.83	21.72	25.23	25.06	32.21
FeO	0.23	0.49	0.52	0.38	0.44	0.49	0.54	0.20	0.15	0.14	0.55	0.57	0.11	bdl	0.19	0.19	0.54
MnO	0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.05	0.02	0.01	bdl	bdl	bdl	bdl	bdl
MgO	0.01	0.05	0.04	0.05	0.04	0.06	bdl	bdl	bdl	bdl	0.05	0.06	bdl	bdl	bdl	0.02	0.04
CaO	12.25	11.38	14.75	10.47	9.88	10.58	16.17	9.66	6.35	4.55	16.80	16.81	6.34	2.29	6.82	6.68	15.50
Na <sub>2</sub> O	4.39	4.86	3.02	5.35	5.54	5.35	2.64	5.96	7.67	8.56	1.92	2.00	7.87	9.79	7.56	7.30	2.77
K <sub>2</sub> O	0.14	0.27	0.08	0.13	0.17	0.18	0.05	0.19	0.30	0.64	0.06	0.03	0.25	0.18	0.20	0.24	0.07
BaO	0.02	0.00	bdl	bdl	0.02	bdl	bdl	bdl	0.02	0.11	bdl	bdl	bdl	bdl	0.03	0.05	bdl
SrO	0.23	0.21	0.15	0.14	0.37	0.37	0.11	0.14	0.23	0.20	0.11	0.11	0.26	0.09	0.12	0.18	0.15
Total	99.55	99.52	100.42	99.37	98.83	99.48	100.63	100.31	100.66	100.59	99.09	98.80	100.41	100.05	100.55	99.16	100.42
An%	60.21	55.51	72.63	51.58	49.12	51.69	76.99	46.71	30.86	21.88	82.58	82.13	30.38	11.33	32.89	33.09	75.26

Note: IPD-intermediate porphyry dike; ME-mafic enclave; QM-quartz monzonite; BT-biotite tonalite; BA-basaltic andesite; PR-Paredones rhyodacite; PBA-Paredones basaltic andesite. Units in wt%.

bdl = below detection limit

TABLE 3. U-Pb GEOCHRONOLOGY

TABLE 3. STD GEONORM-2007																						
Dates (Ma)				Composition								Isotopic ratios										
<sup>206</sup> Pb/ <sup>238</sup> U																						
Fraction	<Th>†	±2σ abs	<sup>206</sup> Pb/ <sup>238</sup> U §	±2σ abs	<sup>207</sup> Pb/ <sup>235</sup> U §	±2σ abs	<sup>207</sup> Pb/ <sup>206</sup> Pb §	±2σ abs	Corr. coef.	% disc #	Th/U ††	Pb* (pg) §§	Pbc (pg)	##Pb*/Pbc †††	<sup>206</sup> Pb/ <sup>204</sup> Pb §§§	<sup>208</sup> Pb/ <sup>206</sup> Pb ##	<sup>206</sup> Pb/ <sup>238</sup> U ###	±2σ %	<sup>207</sup> Pb/ <sup>235</sup> U ###	±2σ %	<sup>207</sup> Pb/ <sup>206</sup> Pb ###	±2σ %
DM2AG33																						
z1	3.901	0.101	3.801	0.102	3.785	1.186	-6.390	743.677	0.257	159.488	0.30	0.13	0.38	0.34	39.6	0.098	0.0005898	2.676	0.0037348	31.393	0.0459	30.815
z3	3.925	0.275	3.841	0.276	3.739	3.154	-61.791	2032.388	0.208	106.217	0.81	0.05	0.32	0.14	25.9	0.267	0.0005961	7.196	0.0036890	84.524	0.0449	83.326
z4	8.701	0.045	8.604	0.045	8.904	0.492	90.671	129.880	0.181	90.510	0.38	0.96	0.57	1.70	123.7	0.124	0.0013356	0.527	0.0088074	5.552	0.0478	5.481
z6	3.920	0.232	3.829	0.234	3.607	2.591	-142.155	1760.775	0.184	102.693	0.57	0.09	0.57	0.153	27.2	0.188	0.0005941	6.108	0.0035587	71.947	0.0435	71.076
z8	4.164	0.242	4.079	0.244	6.752	2.714	1106.828	782.084	0.270	99.631	0.78	0.05	0.28	0.18	27.9	0.256	0.0006330	5.977	0.0066720	40.322	0.0765	39.134
z9	4.014	0.086	3.925	0.087	3.314	1.007	-421.366	784.189	0.260	100.931	0.63	0.10	0.22	0.45	44.1	0.208	0.0006090	2.221	0.0032691	30.437	0.0389	29.936
z10	4.004	0.210	3.907	0.214	4.127	2.852	134.410	1568.242	0.491	97.093	0.40	0.04	0.19	0.21	30.8	0.133	0.0006063	5.472	0.0040726	69.240	0.0487	66.721
DM6AG05																						
z1	4.036	0.017	3.960	0.018	4.142	0.203	111.051	113.222	0.275	96.434	1.08	1.34	0.52	2.59	152.5	0.351	0.0006145	0.443	0.0040873	4.899	0.0483	4.796
z3	4.060	0.059	3.979	0.059	4.436	0.655	259.975	334.716	0.199	98.469	0.90	0.28	0.40	0.70	55.8	0.293	0.0006175	1.482	0.0043781	14.794	0.0514	14.571
z5	4.088	0.096	4.009	0.097	4.744	1.158	395.842	538.717	0.232	98.987	0.95	0.31	0.70	0.44	41.3	0.312	0.0006220	2.414	0.0046827	24.470	0.0546	24.026
z6	4.014	0.044	3.936	0.044	3.659	0.529	-175.359	353.309	0.306	102.244	0.98	0.47	0.47	0.998	71.4	0.319	0.0006107	1.125	0.0036096	14.474	0.0429	14.169
z7	4.136	0.078	4.047	0.079	4.368	0.915	185.133	478.449	0.267	97.814	0.65	0.26	0.50	0.52	48.1	0.213	0.0006280	1.957	0.0043110	20.983	0.0498	20.547
DMN30																						
8_zb	3.847	0.086	3.757	0.087	3.964	1.006	131.552	588.803	0.211	97.144	0.60	0.29	0.69	0.42	42.8	0.197	0.0005829	2.305	0.0039111	25.421	0.0487	25.038
z1	8.443	0.148	8.360	0.148	8.760	1.656	120.087	440.197	0.221	93.038	0.86	1.12	1.93	0.58	49.9	0.278	0.0012977	1.774	0.0086647	18.990	0.0484	18.679
z2	3.879	0.049	3.796	0.049	4.335	0.557	315.066	287.498	0.234	98.795	0.82	0.22	0.27	0.80	62.2	0.269	0.0005890	1.304	0.0042784	12.882	0.0527	12.640
z3	3.879	0.026	3.790	0.026	4.021	0.296	144.761	170.616	0.195	97.382	0.65	0.66	0.47	1.40	98.8	0.212	0.0005880	0.698	0.0039676	7.377	0.0490	7.273
z5	3.902	0.133	3.827	0.135	7.809	1.954	1514.258	441.474	0.544	99.747	1.08	0.10	0.25	0.41	38.8	0.353	0.0005938	3.524	0.0077208	25.124	0.0943	23.394
z6	7.869	0.043	7.789	0.044	8.024	0.617	79.130	180.611	0.233	90.157	0.91	0.52	0.28	1.86	118.8	0.295	0.0012089	0.560	0.0079333	7.716	0.0476	7.605
z7	3.884	0.027	3.792	0.027	4.085	0.323	180.547	179.389	0.354	97.900	0.55	0.28	0.19	1.47	105.1	0.182	0.0005884	0.719	0.0040311	7.922	0.0497	7.697
DM4AG14																						
10_006	3.727	0.115	3.650	0.116	4.052	1.308	250.137	731.668	0.219	98.541	1.02	0.22	0.65	0.34	35.8	0.334	0.0005663	3.170	0.0039983	32.338	0.0512	31.795
10_011	3.741	0.028	3.695	0.028	3.827	0.322	87.807	195.730	0.287	95.792	2.01	1.23	0.65	1.88	98.4	0.653	0.0005734	0.755	0.0037764	8.440	0.0478	8.255
z2	3.725	0.055	3.634	0.055	3.982	0.625	219.736	357.748	0.216	98.346	0.60	1.38	2.18	0.63	55.0	0.196	0.0005639	1.526	0.0039293	15.718	0.0506	15.461
z3	3.724	0.019	3.683	0.019	3.836	0.206	101.205	124.984	0.221	96.361	2.19	2.81	1.04	2.69	129.4	0.709	0.0005715	0.513	0.0037853	5.375	0.0481	5.285
z4	3.727	0.025	3.673	0.025	3.969	0.285	187.961	164.798	0.226	98.046	1.74	0.80	0.43	1.89	103.0	0.567	0.0005699	0.689	0.0039168	7.204	0.0499	7.081
z5	3.766	0.035	3.732	0.035	4.144	0.383	251.211	210.209	0.186	98.515	2.38	1.24	0.83	1.49	77.6	0.771	0.0005790	0.934	0.0040900	9.264	0.0513	9.137
Z8	3.732	0.055	3.703	0.028	3.694	0.350	-2.466	222.780	0.374	250.160	2.57	1.42	0.66	2.15	101.2	0.830	0.0005747	0.768	0.0036446	9.498	0.0460	9.238
DM2AG01																						
z5	3.849	0.080	3.756	0.081	4.266	0.928	302.417	487.568	0.240	98.758	0.51	0.76	1.70	0.44	44.6	0.167	0.0005828	2.144	0.0042101	21.801	0.0524	21.388
z6	3.833	0.011	3.732	0.011	3.994	0.124	165.050	71.459	0.258	97.739	0.23	0.85	0.27	3.12	220.1	0.076	0.0005790	0.302	0.0039408	3.122	0.0494	3.057
z8	3.831	0.052	3.739	0.052	3.867	0.586	84.294	355.513	0.190	95.564	0.55	0.43	0.64	0.67	57.8	0.180	0.0005802	1.398	0.0038156	15.188	0.0477	14.985
z9	3.810	0.029	3.724	0.029	3.532	0.329	-125.806	226.155	0.249	102.960	0.73	0.36	0.28	1.31	92.6	0.240	0.0005779	0.774	0.0034843	9.320	0.0438	9.158
z10	3.814	0.033	3.732	0.033	3.619	0.372	-71.544	247.649	0.223	105.217	0.89	0.26	0.22	1.17	81.7	0.292	0.0005792	0.893	0.0035701	10.296	0.0447	10.134

z11	<b>3.810</b>	<b>0.087</b>	3.728	0.088	3.588	1.019	-89.611	686.796	0.232	104.160	0.85	0.15	0.33	0.44	42.2	0.279	0.0005784	2.357	0.0035395	28.460	0.0444	28.008
z12	<b>3.864</b>	<b>0.093</b>	3.774	0.093	3.941	1.034	107.166	612.532	0.193	96.479	0.61	0.21	0.55	0.39	40.6	0.201	0.0005856	2.476	0.0038885	26.293	0.0482	25.929
z13	<b>3.821</b>	<b>0.072</b>	3.735	0.073	4.093	0.833	220.134	464.189	0.214	98.303	0.77	0.11	0.22	0.52	46.9	0.252	0.0005796	1.944	0.0040395	20.388	0.0506	20.062
z14	<b>3.844</b>	<b>0.115</b>	3.760	0.116	4.572	1.267	456.353	608.194	0.171	99.176	0.80	0.22	0.69	0.32	36.0	0.261	0.0005835	3.075	0.0045132	27.769	0.0561	27.412
DM6AG21																						
8_z001	<b>3.911</b>	<b>0.063</b>	3.834	0.065	4.035	3.883	125.949	2259.073	0.281	96.956	1.02	0.12	1.00	0.12	24.2	0.333	0.00059493	1.700	0.0039821	96.426	0.0486	95.963
8_z010	<b>4.063</b>	<b>0.059</b>	3.986	0.061	4.138	3.623	93.657	2067.319	0.284	95.744	1.05	0.09	0.68	0.13	24.9	0.341	0.00061853	1.538	0.0040839	87.716	0.0479	87.291
z1	<b>4.195</b>	<b>0.209</b>	4.122	0.217	3.494	5.889	-411.126	4335.140	0.575	101.003	1.18	0.03	0.31	0.10	23.4	0.386	0.00063969	5.262	0.0034472	168.812	0.0391	165.840
z2	<b>3.913</b>	<b>0.143</b>	3.838	0.149	4.371	5.759	308.945	2964.159	0.489	98.758	1.09	0.04	0.40	0.09	22.7	0.356	0.00059556	3.889	0.0043143	132.036	0.0526	130.179
z3	<b>4.062</b>	<b>0.100</b>	3.990	0.104	5.333	3.747	663.403	1481.748	0.501	99.399	1.18	0.05	0.31	0.15	25.6	0.385	0.00061915	2.607	0.0052665	70.434	0.0617	69.164
z4	<b>4.245</b>	<b>0.101</b>	4.191	0.105	5.628	5.538	673.813	2092.798	0.332	99.378	1.75	0.09	0.83	0.11	22.9	0.569	0.00065032	2.509	0.0055585	98.660	0.0620	97.855
z5	<b>4.099</b>	<b>0.078</b>	4.033	0.082	7.316	3.152	1287.811	826.375	0.408	99.687	1.40	0.07	0.37	0.18	26.66	0.454	0.00062583	2.033	0.0072307	43.238	0.0838	42.450
z6	<b>4.031</b>	<b>0.077</b>	3.968	0.079	4.656	2.349	376.558	1119.163	0.432	98.946	1.48	0.08	0.35	0.23	29.02	0.483	0.00061578	1.993	0.0045961	50.573	0.0542	49.744
DM5AG32																						
z2	<b>3.663</b>	<b>0.070</b>	3.598	0.070	3.860	0.779	170.484	465.555	0.197	97.890	1.40	0.52	0.88	0.59	46.7	0.458	0.00055826	1.951	0.0038083	20.232	0.0495	19.939
z4	<b>3.842</b>	<b>0.095</b>	3.767	0.096	4.303	1.120	315.171	574.345	0.370	98.805	1.11	0.18	0.38	0.48	42.8	0.364	0.00058458	2.537	0.0042464	26.082	0.0527	25.252
z5	<b>3.660</b>	<b>0.037</b>	3.568	0.038	3.886	0.420	205.784	246.961	0.215	98.266	0.55	0.39	0.43	0.91	71.8	0.181	0.00055368	1.052	0.0038348	10.822	0.0503	10.646
z6	<b>3.604</b>	<b>0.072</b>	3.512	0.073	1.956	1.040	-1668.366	1800.471	0.577	100.211	0.54	0.17	0.27	0.61	54.9	0.179	0.00054499	2.091	0.0019278	53.223	0.0257	52.044
z8	<b>3.695</b>	<b>0.083</b>	3.611	0.084	3.888	1.033	178.901	595.787	0.487	97.981	0.82	0.19	0.36	0.53	47.4	0.268	0.00056038	2.336	0.0038367	26.612	0.0497	25.557
DM8AG44																						
z1	<b>3.720</b>	<b>0.110</b>	3.639	0.109	2.609	1.269	-870.952	1385.057	0.242	100.418	0.91	0.18	0.53	0.35	37.1	0.299	0.00056468	3.007	0.0025732	48.709	0.0331	48.070
z2	<b>3.766</b>	<b>0.128</b>	3.683	0.128	4.177	1.452	299.198	780.072	0.230	98.769	0.84	0.15	0.50	0.30	34.4	0.274	0.00057147	3.474	0.0041221	34.832	0.0523	34.199
z3	<b>3.602</b>	<b>0.126</b>	3.508	0.127	2.551	1.440	-830.850	1598.996	0.183	100.422	0.47	0.25	1.02	0.25	33.4	0.156	0.00054427	3.626	0.0025151	56.533	0.0335	55.982
z4	<b>7.588</b>	<b>0.323</b>	7.502	0.324	8.970	3.978	423.264	969.511	0.298	98.228	0.72	0.26	1.08	0.24	31.6	0.234	0.00116436	4.326	0.0088736	44.540	0.0553	43.446
z5	<b>3.703</b>	<b>0.111</b>	3.613	0.112	4.271	1.250	392.942	646.460	0.213	99.080	0.64	0.19	0.59	0.32	36.3	0.211	0.0005607	3.089	0.0042155	29.317	0.0546	28.816
z6	<b>3.802</b>	<b>0.104</b>	3.711	0.105	5.313	1.420	809.055	536.205	0.456	99.541	0.56	0.14	0.36	0.39	40.9	0.185	0.00057577	2.827	0.0052463	26.793	0.0661	25.628
z7	<b>3.793</b>	<b>0.132</b>	3.705	0.133	4.344	1.712	374.544	865.624	0.331	99.011	0.68	0.24	0.83	0.29	34.57	0.224	0.00057492	3.584	0.0042872	39.498	0.0541	38.461
DM3AG15																						
z1	<b>3.629</b>	<b>0.079</b>	3.558	0.079	3.690	0.879	90.481	555.046	0.250	96.068	1.23	0.23	0.45	0.52	44.0	0.402	0.00055207	2.226	0.0036402	23.879	0.0478	23.423
z2	<b>3.568</b>	<b>0.101</b>	3.491	0.102	2.827	1.226	-533.132	1144.155	0.288	100.655	1.06	0.34	0.89	0.38	38.1	0.346	0.00054175	2.925	0.002788	43.431	0.0373	42.681
z4	<b>4.794</b>	<b>0.163</b>	4.716	0.164	5.979	1.849	549.350	664.956	0.215	99.142	1.01	0.20	0.66	0.31	34.3	0.328	0.00073186	3.475	0.0059054	31.010	0.0585	30.452
z6	<b>3.667</b>	<b>0.074</b>	3.576	0.075	3.602	0.828	20.859	546.193	0.184	82.856	0.58	0.50	1.11	0.45	44.7	0.191	0.0005549	2.085	0.0035536	23.041	0.0465	22.749
z7	<b>3.665</b>	<b>0.047</b>	3.579	0.048	3.627	0.540	35.652	349.437	0.277	89.960	0.76	0.90	1.14	0.79	62.5	0.249	0.00055541	1.333	0.0035789	14.909	0.0468	14.595
z8	<b>3.657</b>	<b>0.234</b>	3.583	0.234	4.045	2.613	288.694	1456.476	0.200	98.759	1.13	0.17	1.04	0.17	26.6	0.371	0.00055593	6.536	0.0039916	64.721	0.0521	63.733
z9	<b>3.735</b>	<b>0.111</b>	3.653	0.112	4.783	1.265	618.101	560.060	0.243	99.409	0.90	0.20	0.58	0.35	36.79	0.294	0.0005669	3.055	0.0047215	26.520	0.0604	25.946
z10	<b>3.699</b>	<b>0.170</b>	3.634	0.170	4.330	1.926	410.583	979.703	0.214	99.115	1.43	0.16	0.62	0.25	30.07	0.467	0.0005639	4.680	0.0042731	44.568	0.0550	43.806

† Corrected for initial Th/U disequilibrium using radiogenic 208Pb and Th/U[magma] = 3.50000.

§ Isotopic dates calculated using the decay constants  $\lambda_{238} = 1.55125\text{E-}10$  and  $\lambda_{235} = 9.8485\text{E-}10$  (Jaffey et al. 1971).

# % discordance =  $100 - (100 * (^{206}\text{Pb}/^{238}\text{U date}) / (^{207}\text{Pb}/^{206}\text{Pb date}))$

†† Th contents calculated from radiogenic 208Pb and the 207Pb/206Pb date of the sample, assuming concordance between U-Th and Pb systems.

§§ Total mass of radiogenic Pb.

## Total mass of common Pb.

††† Ratio of radiogenic Pb (including  $^{208}\text{Pb}$ ) to common Pb.

§§§ Measured ratio corrected for fractionation and spike contribution only.

### Measured ratios corrected for fractionation, tracer and blank.

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TABLE 4. <sup>40</sup>Ar/<sup>39</sup>Ar GEOCHRONOLOGY FOR DON MANUEL PRINCIPAL BASALTIC ANDESITE DIKES

Sample	Material	J	±1σ	Integrated		%radiogenic		Plateau	±1σ w/o J	±1σ w/ J	MSWD	Prob.	steps	n/n-total	%gas	mol <sup>39</sup> Ar	Ca/K	±1σ Ca/K	Isochron							
				age (Ma)	±1σ	<sup>40</sup> Ar	int. <sup>40</sup> Ar* / <sup>39</sup> Ar <sub>K</sub>												age (Ma)	±2σ	±2σ (%)	<sup>40</sup> Ar/ <sup>36</sup> Ar(i)	±2σ	MSWD	p	n
DM4AG28	Groundmass	2.49E-04	1.45E-06	4.7	0.2	19.2	10.380	3.85	0.18	0.19	1.9	0.1	5-9	5/13	70.6	4.54E-16	2.82	0.30	4.01	0.61	10.0	295	14	2.3	0.08	5
DM7AG26	Groundmass	2.62E-04	9.50E-07	3.8	0.1	59.9	8.129	3.60	0.05	0.06	1.3	0.26	7-10	4/12	50	1.75E-15	2.17	0.10	3.54	0.47	9.4	308	75	2.0	0.14	4

Notes: Samples were irradiated in the Oregon State University reactor, Cd-shielded facility. Alder Creek sanidine (1.2056 ± 0.0019 (1σ) Ma, Renne et al. 2011) was used to establish neutron flux values (J). Decay constants are listed in Renne et al. (2011).

Nucleogenic production ratios:

<sup>39</sup> Ar/ <sup>37</sup> Ar)Ca	2.64 × 10 <sup>-4</sup>
<sup>39</sup> Ar/ <sup>37</sup> Ar)Ca	6.5 × 10 <sup>-4</sup>
<sup>39</sup> Ar/ <sup>37</sup> Ar)Ca	0.196 ± 0.00816 × 10 <sup>-4</sup>
<sup>40</sup> Ar/ <sup>39</sup> Ar)K	8.5 × 10 <sup>-3</sup>
<sup>39</sup> Ar/ <sup>39</sup> Ar)K	1.22 ± 0.0027 × 10 <sup>-2</sup>
<sup>39</sup> Ar/ <sup>39</sup> Ar)Cl	2.629 ± 0.011 × 10 <sup>2</sup>
<sup>37</sup> Ar/ <sup>39</sup> Ar to Ca/K	1.96
<sup>38</sup> Ar/ <sup>39</sup> Ar to Cl/K	2.9

Isotopic constants and decay rates:

λ( <sup>40</sup> K <sub>d</sub> )/yr	5.757 ± 0.016 × 10 <sup>-11</sup>
λ( <sup>40</sup> K <sub>p</sub> )/yr	4.955 ± 0.013 × 10 <sup>-10</sup>
λ( <sup>37</sup> Ar)/d	1.983 ± 0.0045 × 10 <sup>-2</sup>
λ( <sup>39</sup> Ar)/d	7.068 ± 0.0788 × 10 <sup>-6</sup>
λ( <sup>36</sup> Cl)/d	6.308 ± 0 × 10 <sup>-9</sup>
( <sup>40</sup> Ar/ <sup>36</sup> Ar) <sub>Atm</sub>	298.56 ± 0.31
( <sup>40</sup> Ar/ <sup>38</sup> Ar) <sub>Atm</sub>	1583.5 ± 2.5
<sup>40</sup> K/K <sub>Total</sub>	0.01167 ± 0.00002



# GSA Data Repository

## Geology of the Don Manuel igneous complex, central Chile: relationship between igneous processes in volcanic and porphyry copper systems

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DR4. <sup>40</sup>Ar-<sup>39</sup>Ar Geochronology:

- Sample preparation
- <sup>40</sup>Ar-<sup>39</sup>Ar geochronology methods

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Figure DR6. Internal ductile contact within a composite intermediate porphyry dike (IPD).

### References for Data Repository

## **DR1. Whole rock geochemistry methods.**

A mass of  $0.1 \text{ g} \pm 0.002$  of sample was measured, placed in a platinum crucible with  $0.4 \text{ g} \pm 0.005$  lithium metaborate flux (Alfa Aesar Spectroflux 100B) and 0.5 mL of lithium iodide 25% solution (Alfa Aesar) that was used as a non-wetting agent, and fused in a Claisse FLUXY automated fusion system. The melt was automatically poured into a Teflon beaker with 50 mL of 4%  $\text{HNO}_3$  acid solution and stirred until completely dissolved. One mL of 100 ppm rhodium spike solution was added as an internal standard. All samples were diluted to 100 mL with 18.2 M $\Omega$  deionized water, resulting in a spiked rock solution in 2%  $\text{HNO}_3$ . Solutions were then analyzed for bulk composition using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) using a JY Horiba ULTIMA2. Analyses of trace and rare earth elements were performed on some solutions that were first further diluted by 10 times with 2%  $\text{HNO}_3$  spiked to correct for instrument drift at low and high masses (5 ppb In and Tl internal standards). These solutions were analyzed using a Thermo Elemental X Series (X7) ICP-MS system. Calibration was carried out using reagent blank and international certified reference materials (CRM) (DTS-1, W2, BIR1, MRG1, JA2, STM-1 and JG3) and JA2, JG1a and JB1a as secondary standards. The relative analytical errors ( $\pm 2\sigma$ ) for major elements were less than 1% (with the exception of Fe and Na, where the error was 2%) and about 5% for trace elements. The loss on ignition determination error is about 10%.

### **DR3. Zircon U-Pb geochronology**

#### *Sample preparation*

Four samples were split using a hydraulic rock splitter to reduce the sample to manageable fragments for the jaw-crusher. The jaw-crusher is used to reduce the split sample to a size suitable for sieving. Sample concentrates were prepared from sieve fractions from 50 to 250  $\mu\text{m}$  using a hand magnet, heavy liquid (LST, density at 2.85 g/mL), and a Frantz magnetic separator. Approximately 50 zircon grains from each sample were hand-picked from each concentrate. Grains were photographed in transmitted light (Figure DR3.1).

#### *Zircon characterization*

Grains were photographed in transmitted light (Figure DR3.1). Additional zircons from each sample were mounted in epoxy disks and polished to expose a cross-section through the grain. Zircons were then imaged in BSE and Cathodoluminescence (CL) at the British Geological Survey, and at the University of Bristol to (Figure DR3.2). CL imaging was done to texturally characterize each sample's zircon population. Zircons typically showed mixed populations of: 1) multifaceted crystals with large, rounded and resorbed antecrystic cores with late-stage discordant rims; and 2) elongate or prismatic zircons which showed simpler growth evolution within their CL images. For the zircon grains or fragments that were dated we favoured the selection of elongate prismatic morphologies - as these were likely to contain the simplest growth histories that predated emplacement, and therefore give the best approximation of the emplacement age of their host intrusion. As DMIC zircons are typically small in size and have low concentrations of radiogenic Pb, we generally favoured dating whole zircons or fragments rather than those that had been CL imaged due to the reduced mass resulting from polishing.

#### *Methods*

Sample preparation and analyses for Chemical Abrasion Isotope Dilution Thermal Ionisation Mass spectrometry were carried out at the NERC Isotope Geosciences Laboratory (NIGL), British Geological Survey, Keyworth, UK. Methodology and instrumentation follows those described by Tapster et al. (2016). The important points are outlined here: Zircons were thermally annealed and chemically abraded prior to dissolution (Mattinson, 2005); The mixed  $^{205}\text{Pb}$ – $^{233}\text{U}$ – $^{235}\text{U}$  EARTHTIME solutions (ET535; (Condon et al., 2015; McLean et al., 2015); Common Pb was attributed to the NIGL laboratory blank isotopic composition and associated uncertainty based upon

repeat analysis of total procedural blanks during the analytical period, U blanks were assigned a value of  $0.1 \pm 0.01$  pg ( $1\sigma$ ); Processing of isotope measurements, data reduction, error propagation, and date calculation was conducted using the TRIPOLI software package (Bowring et al., 2011) and ET\_Redux and related algorithms (McLean et al., 2011);  $^{206}\text{Pb}/^{238}\text{U}$  zircon dates were corrected for initial Th/U disequilibrium between the crystallising zircon and its host magma, which leads to the preferential incorporation of  $^{238}\text{U}$  and exclusion of  $^{230}\text{Th}$ , a daughter isotope within the decay series of  $^{238}\text{U}$  to  $^{206}\text{Pb}$ . In turn, this leads to an eventual deficit in  $^{206}\text{Pb}$  within the analysed zircons and younger apparent dates (Schärer, 1984). For the correction we assumed a  $\text{Th}/\text{U}_{(\text{melt})} = 3.5$  and concordance between the  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{208}\text{Pb}/^{232}\text{Th}$  systems. Using the  $\lambda^{230}\text{Th}$  of Cheng et al., (2000), and the  $\lambda^{238}\text{U}$  of Jaffey et al., (1971) this correction results in an increase in  $^{206}\text{Pb}/^{238}\text{U}$  dates on the order of ca. 100 kyr for individual fractions.

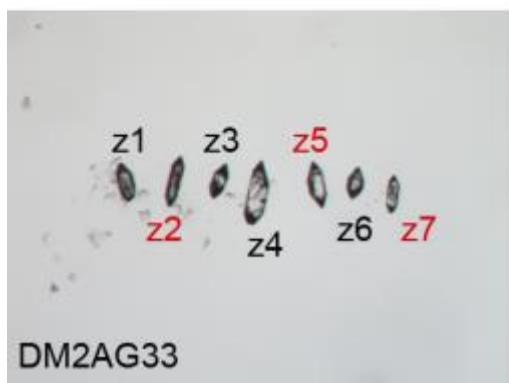
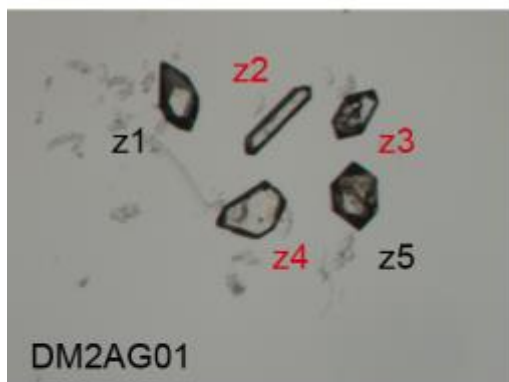
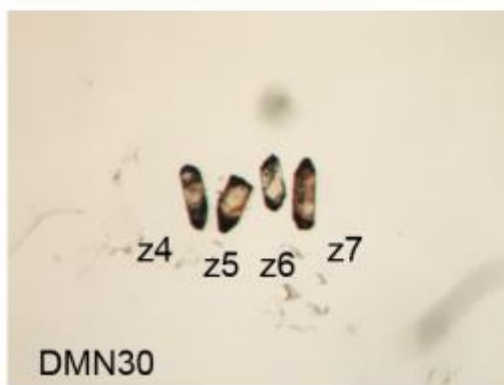
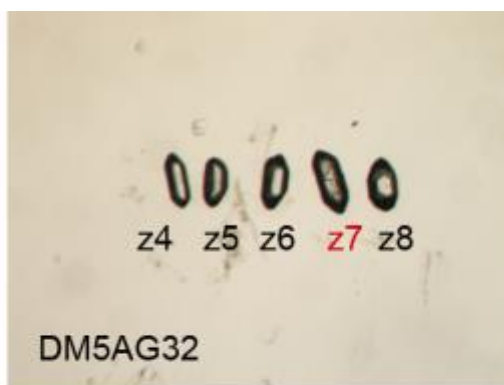
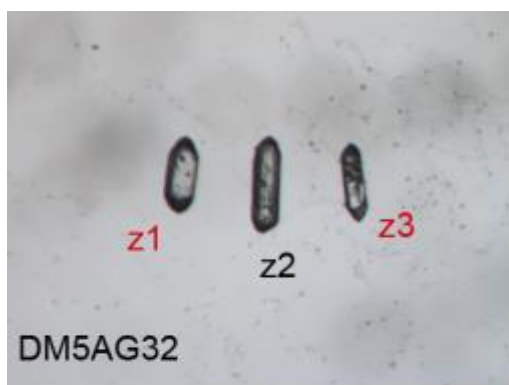


Figure DR3.1: Transmitted light images of annealed zircons. Red labels indicated zircons that were selected but were not analyzed. FOV=1.2 mm. Not all samples shown.

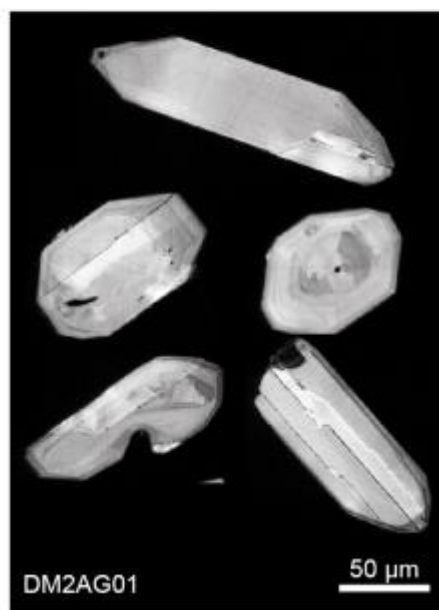
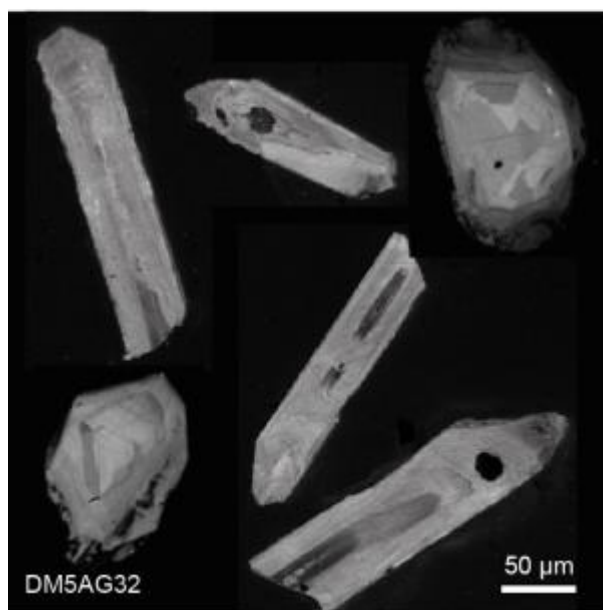
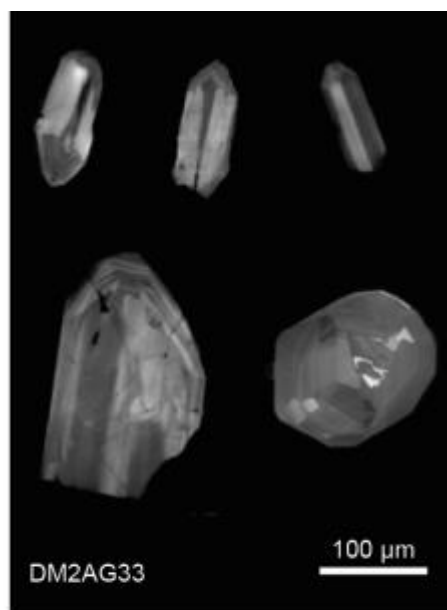
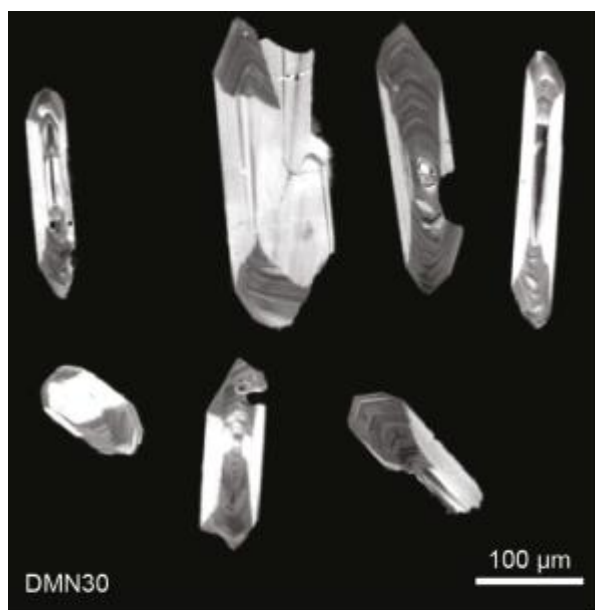


Figure DR3.2: CL images of representative zircons from dated samples.  
Not all samples shown.

## DR4. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology

### *Sample preparation*

Samples were trimmed to remove any weathering/staining using a diamond water saw. Six samples were split using a hydraulic rock splitter to reduce the sample to manageable fragments for the jaw-crusher. The jaw-crusher is used to reduce the split sample to a size suitable for sieving. Samples were sieved to obtain a 250-500  $\mu\text{m}$  aliquot. They were then passed over with a strong hand magnet to remove any metal particles introduced during crushing. Dust was removed by washing the samples in deionized water in an ultrasonic bath for 10 minutes. Samples were leached in 3N  $\text{HNO}_3$  for 20 minutes in an ultrasonic bath at 50°C. This was repeated until a clear solution was obtained. Samples were then rinsed with deionized water and then washed with deionized water in an ultrasonic bath for 10 minutes. Samples were then hand-picked under a binocular microscope and care was taken to remove all phenocrysts and altered grains. For each sample 1 g of groundmass separate was attained.

### *Methods*

Samples and neutron flux monitors were placed in aluminium discs and stacked in quartz tubes. The relative positions of wells in the discs were precisely measured for later reconstruction of neutron flux gradients. The sample package was irradiated in the Oregon State University reactor, Cd-shielded facility. Alder Creek sanidine ( $1.2056 \pm 0.0019$  ( $1\sigma$ ) Ma, (Renne et al., 2011)) was used to monitor  $^{39}\text{Ar}$  production and establish neutron flux values (J) for the samples. Gas was extracted from samples via step-heating using a mid-infrared (10.6  $\mu\text{m}$ )  $\text{CO}_2$  laser with a non-gaussian, uniform energy profile and a 3.5 mm beam diameter. The samples were housed in a doubly-pumped ZnS-window laser cell and loaded into a copper planchette containing four 2.6  $\text{cm}^2$  square wells. Liberated argon was purified of active gases, e.g.,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , using three Zr-Al getters; one at 16°C and two at 400°C. Data were collected on a GVi instruments ARGUS V multi-collector mass spectrometer using a variable sensitivity faraday collector array in static collection (non-peak hopping) mode (Mark et al., 2009; Sparks et al., 2008). Time-intensity data are regressed to  $t_0$  with second-order polynomial fits to the data. Mass discrimination was monitored on a daily basis by comparison to running-average values of an air standard. The average total system blank for laser extractions, measured between each sample run, was  $2 \times 10^{-15}$  mol  $^{40}\text{Ar}$ ,  $1 \times 10^{-17}$  mol  $^{39}\text{Ar}$ ,  $2 \times 10^{-17}$  mol  $^{36}\text{Ar}$ . All data are blank, interference and mass discrimination corrected using the *MassSpec* software package (*MassSpec*, version 8.058, authored by Al Deino, Berkeley Geochronology Center, Version 8.058).

--- Atmospheric argon ratios and discrimination ---

$(^{40}\text{Ar}/^{36}\text{Ar})_{\text{atm}}$        $298.56 \hat{\pm} 0.31$

$(^{40}\text{Ar}/^{38}\text{Ar})_{\text{atm}}$        $1583.5 \hat{\pm} 2.5$

--- Minor irradiation parameters (see also Irradiation Data File) ---

$(^{38}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$        $0.0000196 \hat{\pm} 8.160000\text{e-}7$

$(^{38}\text{Ar}/^{39}\text{Ar})_{\text{K}}$        $0.0122 \hat{\pm} 0.000027$

$P(^{36}\text{Cl}/^{38}\text{Cl})$        $262.9 \hat{\pm} 1.1$

--- Decay constants ---

$\text{Lambda } ^{40}\text{K epsilon}$      $5.757000\text{e-}11 \pm 1.600000\text{e-}13$

$\text{Lambda } ^{40}\text{K Beta}$        $4.955000\text{e-}10 \pm 1.340000\text{e-}12$

$\text{Lambda } ^{37}\text{Ar}$              $0.01983 \pm 0.0000454$

$\text{Lambda } ^{39}\text{Ar}$              $7.068000\text{e-}6 \pm 7.882200\text{e-}8$

$\text{Lambda } ^{36}\text{Cl}$              $6.308000\text{e-}9 \pm 0$



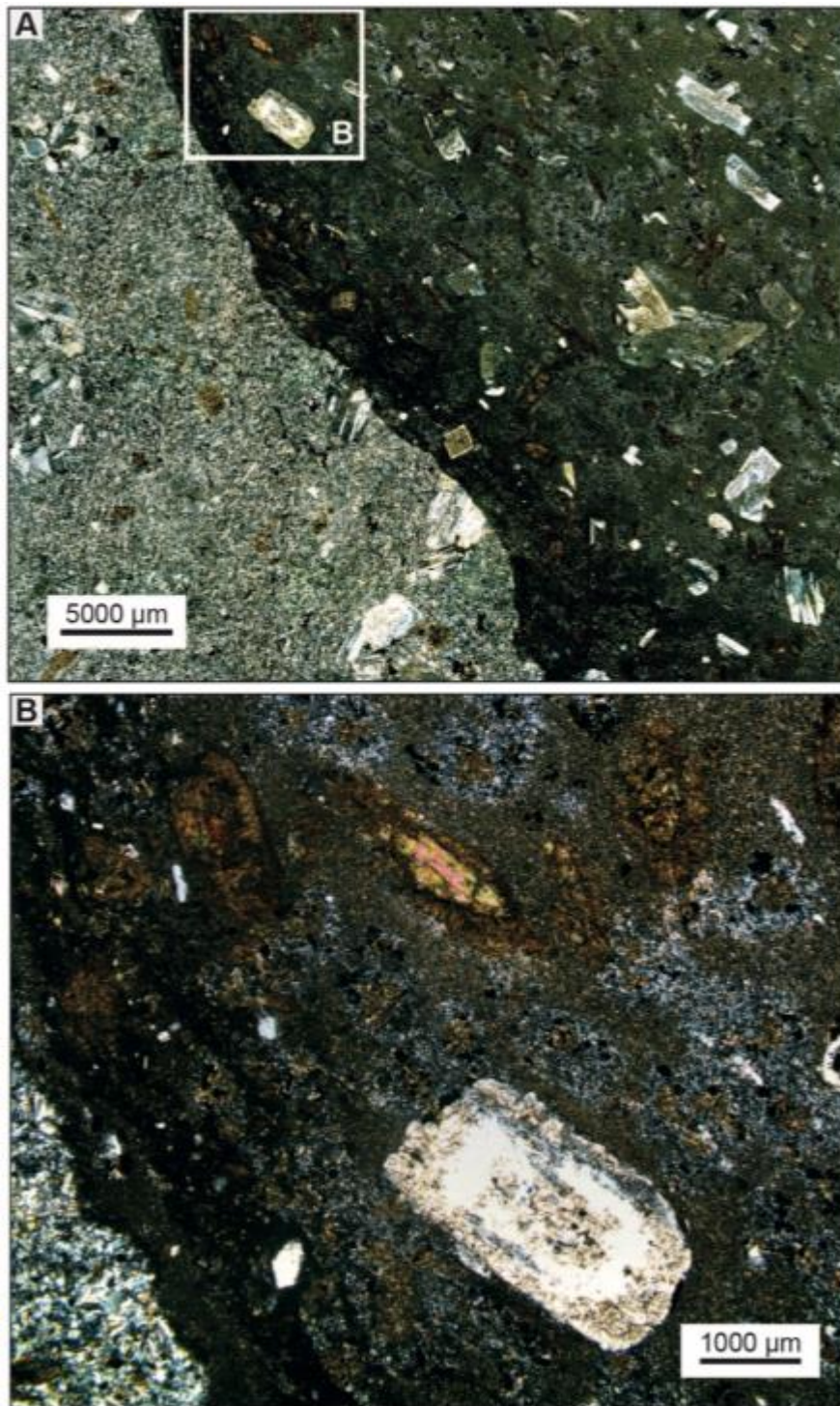


Figure DR5. (A) Mafic enclave in an intermediate porphyry dike showing plagioclase phenocryst likely entrained. (B) Inset showing significant secondary biotite alteration of mafic phases and groundmass.

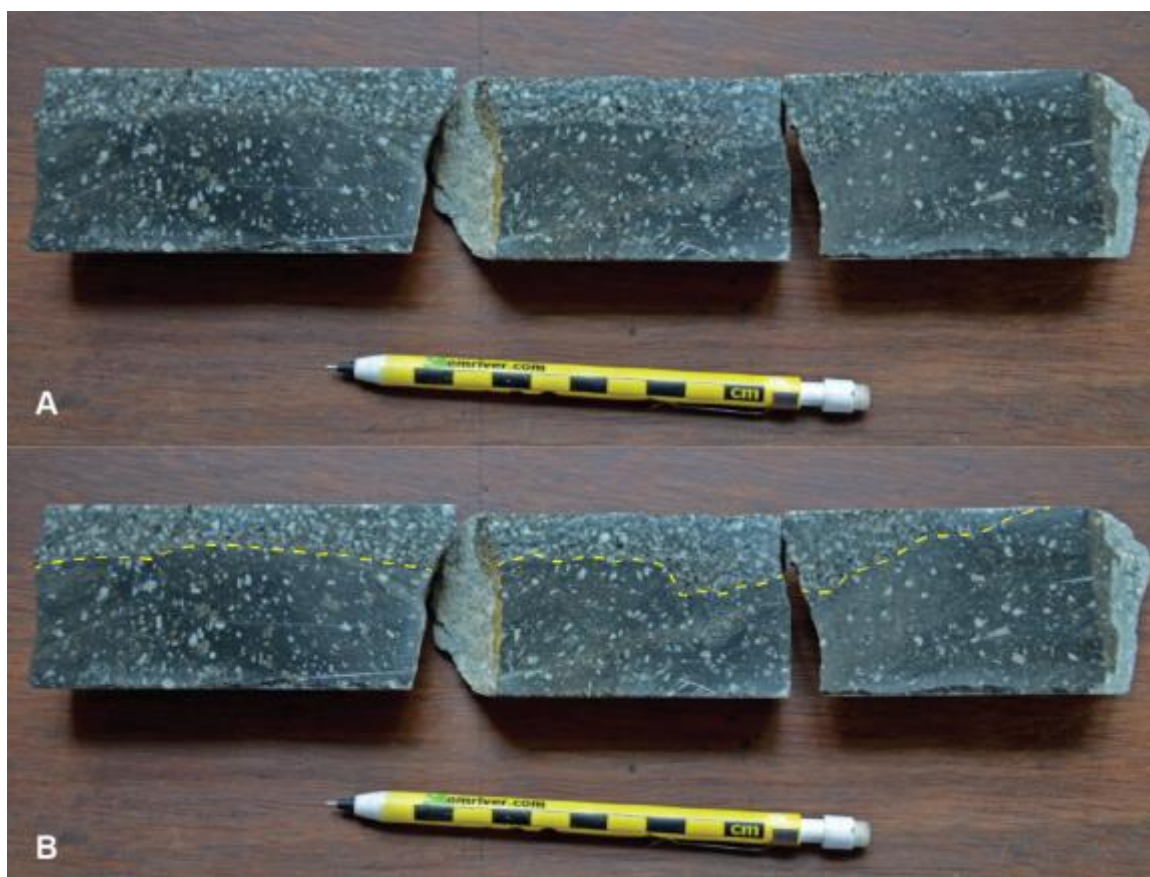


Figure DR6. (A) Internal ductile contact within a composite intermediate porphyry dike (IPD). Yellow dashed line follows the contact (B).

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